Enyl and dienyl complexes of molybdenum

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ENYL AND DIENYL COMPLEXES OF MOLYBDENUM

Submitted by

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CONTENTS

ABBREVIATIONS

Ac	acetate
acac	acetylacetonate
bipy	2,2'-bipyridyl
bpma	bis(2-pyridylmethyl)amine
Bu	butyl
cod	cyclooctadiene
Cp	cyclopentadienyl
dien	diethylenetriamine
dme	dimethoxyethane
DMSO	dimethylsulphoxide
dppe or diphos	1,2-bis(dimethlphosphino)ethane
Et	ethyl
FMO	Frontier Molecular Orbital
h	hour
HOMO	Highest Occupied Molecular Orbital
I.R.	Infra-red
LUMO	Lowest Unoccupied Molecular Orbital
Me	methyl
NMR	Nuclear Magnetic Resonance
pda	pentan-2,4-dionate
Ph	phenyl
phen	1,10-phenanthroline
ppm	parts per million
Pr	propyl
py	pyridine

ABBREVIATIONS (cont.)

pz	pyrazolyl
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine

EXPERIMENTAL DETAILS

All reagents used were of standard laboratory grade and were used without further purification. Reaction solvents were dried over 4Å molecular sieves except for THF, ether and toluene which were freshly distilled over sodium benzophenone when required. All reaction solvents were deoxygenated with dry dinitrogen gas prior to use and all reactions were performed under dinitrogen gas dried by passage through concentrated sulphuric acid. Solvents employed in column chromatography were distilled before use. Merck 60G silica gel was used for column chromatography along with SiO_2 TLC plates.

Infra-red spectra were recorded on a Perkin-Elmer 1310 machine in the range 4000-600cm^{-1} as Nujol mulls between sodium chloride plates except where otherwise noted.

NMR spectra were obtained on a Jeol GX270 spectrometer operating at 270MHz for ^{1}H and 68MHz for ^{13}C NMR. All spectra were recorded at room temperature in standard deuterated solvents and δ values are quoted as shifts downfield from $SiMe_4$ as internal standard.

Mass spectra were recorded on a VG 7070E mass spectrometer.

SECTION 1

SUMMARY

1 SUMMARY

Reaction of 3-chloro-2-chloromethylpropene with $[Mo(NCMe)_3(CO)_3]$ yields the known complex $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (**1**). Direct reaction of this complex with a range of potentially bi- and tri-dentate N- and P-donor ligands did not afford pure products. This is believed to be due to the lability of chlorine in the $-CH_2Cl$ moiety. However, the complex $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (**3**) was prepared from the reaction of $[Mo(bipy)(CO)_4]$ with 3-chloro-2-chloromethylpropene. Reaction of (**1**) with Ph_4AsCl or Et_4NCl in basic methanol solution at room temperature resulted in conversion of the $-CH_2Cl$ moiety to $-CH_2OMe$ and isolation of the product $R_4X[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$ (R=Ph, X=As (**6**) ; R=Et, X=N (**9**)). The structure of (**9**) was confirmed by an X-ray crystal structure determination, which showed that the anion is based on a face-shared bioctahedral arrangement with allyl groups occupying the axial positions on each octahedron. Treatment of (**6**) with either HCl gas or aqueous HCl did not cleave the methoxy group from the allyl moiety and afford tractable products. Attempts were made to prepare η^4-trimethylenemethane analogues by abstraction of chlorine from the $-CH_2Cl$ substituent on the allyl group of (**1**) and (**3**), and a proton from the -Me group in the η^3-2-MeC_3H_4 unit in $[Mo(bpma)(CO)_2(\eta^3\text{-}2\text{-}MeC_3H_4)][PF_6]$ (bpma=bis(2-pyridylmethyl)amine) (**11**). Reactions with silver trifluoroacetate gave trifluoroacetate substituted analogues whereas attempts at the protonation of (**11**) using lithium bis(trimethylsilyl)amide resulted in decomposition. Thermolysis of the neutral complex $[MoCl(bipy)(CO)_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$ (bipy=2,2'-bipyridyl) (**12**) in a boiling xylene/pyridine mixture also failed to yield an η^4-$CH_2C(CH_2)_2$ containing product.

The η^3-butadienyl complexes $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(COR)C{=}CH_2\}]$ (R=OMe (**16**), OEt (**17**), NHEt (**18**)) were prepared by the reaction of

$Ph_4P[MoCl(bipy)(CO)_3]$ with $ClCH_2C{\equiv}CCH_2Cl$ in 30:1 $MeOH/H_2O$ or $EtOH/H_2O$ solutions (for complexes (**16**) and (**17**) respectively) or 2:1 THF/MeOH containing $EtNH_2$ (complex (**18**)). Reaction of these complexes with molecular bromine in CH_2Cl_2 at -78°C yielded the tribrominated organic products $BrCH_2C(COR){=}C(Br)CH_2Br$ (R=OMe (**19**), OEt (**20**), NHEt (**21**)). However, the complexes were found to be unreactive towards mineral acids, triphenylphosphine, or the anion of dimethylmalonate using conditions under which their η^3-allyl analogues readily react. The preparation of $PhCH(OH)C{\equiv}CCH_2OH$ (**22**) was achieved from the reaction between propargyl alcohol, magnesium ethyl bromide and benzaldehyde. Compound (**22**) was then converted to $PhCH(Cl)C{\equiv}CCH_2Cl$ (**23**) by reaction with thionyl chloride and pyridine but the reaction of (**23**) with $Ph_4P[MoCl(bipy)(CO)_3]$ (**15**) in aqueous EtOH yielded an unidentified mixture of Mo products rather than the desired 1-substituted butadienyl complex, $[MoCl(bipy)(CO)_2\{\eta^3\text{-}(Ph)CHC(CO_2Et)C{=}CH_2\}]$.

An entry into analogues of complexes (**16-18**), containing a less sterically hindered η^3-butadienyl moiety was sought as complexes such as $[MoCl(L)_2(CO)_2\{\eta^3\text{-}RCHCHC{=}CH_2\}]$ (R=H, Ph; $(L)_2$=bidentate, $(NCMe)_2$), would be expected to show a greater reactivity towards nucleophiles and electrophiles. In the first route the new complex $[MoCl(bipy)(CO)_2\{\eta^3\text{-}(Ph)CHCHC{=}O\}]$ (**32**) was prepared and characterised from the reaction of molybdenum hexacarbonyl and cinnamoyl chloride in refluxing THF. However, Wittig and Perkin reactions on this complex failed, as did the reaction with the anion of trimethylphosphonoacetate. As an alternative route, abstraction of HCl from the complex $[MoCl(L)_2(CO)_2\{\eta^3\text{-}CH_2CHCHCH_2Cl\}]$ provides another possible entry into unsubstituted η^3-butadienyl complexes. However, attempts to prepare such a complex from the reactions between *cis*- and *trans*-1,4-dichloro-2-butene and $[Mo(CO)_6]$, $[Mo(NCMe)_3(CO)_3]$, $[Mo(bipy)(CO)_4]$ or $Ph_4P[MoCl(bipy)(CO)_3]$ did not produce the required starting materials. The reaction between $[Mo(NCMe)_3(CO)_3]$ and

3,4-dichloro-2-butene gave rise to an unexpected product formulated as $[MoCl_2(NCMe)(CO)_2(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)]$ (**33**). Derivitisation of (**33**) by reaction with pyridine yielded $[MoCl_2(py)_2(CO)_2\{\eta^2\text{-}CH_2{=}CHCH{=}CH_2\}]$ (**34**), whereas reaction with 2-methoxypyridine led only to disproportionation and the isolation of $[MoCl_3(NCMe)_3]$ and $[Mo(CO)_6]$. Monodentate phosphines caused (**33**) to decompose and the attempted substitution of the η^4-butadiene group in this complex by 1,4-diphenyl-1,3-butadiene was not successful. Reactions with diethylacetylenedicarboxylate and diphenylacetylene led to mixtures of complexes rather than the expected Diels-Alder ($4\pi + 2\pi$) adduct. Complex (**33**) with 3 equivalents of molecular bromine at -40°C led to the isolation of a mixture of *cis*- and *trans*-1,4-dibromo-2-butene, providing some corroboration of the proposed structure for complex (**33**). An attempt to prepare the PrCN analogue of complex (**33**) proved to be unsuccessful, however $[MoCl_3(NCPr)_3]$ (**36**) and $[Mo(CO)_6]$ were obtained from the reaction mixture. Crystals of (**36**) suitable for an X-ray crystallographic study were collected and the structure solved to show a *mer*-octahedral geometry.

SECTION 2

TRANSITION METAL η^3-ALLYL COMPLEXES

2 TRANSITION METAL η^3-ALLYL COMPLEXES

Transition metal η^3-allyl complexes have proved to be a useful and versatile class of compounds, particularly in the area of organic synthesis where their ability to selectively react with both nucleophiles and electrophiles has led to the formation of highly specific organic molecules *via* the creation of new carbon-carbon bonds.

The first η^3-allyl transition metal complex was prepared in 1958 by Jonassen *et al*[1], from the reaction between potassium tetracarbonylcobaltate(1-), glacial acetic acid and butadiene, which gave rise to the cobalt complex $[Co(CO)_3(\eta^3\text{-}1\text{-}MeC_3H_4)]$. Subsequently, η^3-allyl complexes of almost all transition metals have been prepared and their potential in organic synthesis realised in many instances.

2.1 Methods of Preparation of Transition Metal η^3-Allyl Complexes

Transition metal η^3-allyl complexes have been prepared by a wide variety of routes. Generally, however these fall into two main categories:

(i) direct reaction of a metal complex with a compound containing an allylic or potential allylic moiety and,

(ii) reaction upon an organic ligand already attached to the metal leading to its conversion to an η^3-allyl system.

Some of the major routes are detailed on the next page.

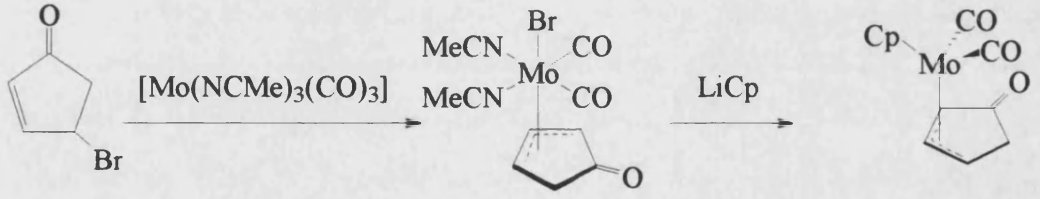
2.1.1 By reaction of allylic compounds with transition metal complexes

The reaction of allyl halides with low valent transition metal complexes is probably the most widely used route into η^3-allyl complexes[2-8]. Some examples are shown below **(Scheme 2.1.1)**.

Scheme 2.1.1

$$[Mo(NCMe)(CO)_3] + CH_2{=}CHCH_2Cl \xrightarrow[-MeCN]{-CO} [MoCl(NCMe)_2(CO)_2(\eta^3\text{-}C_3H_5)]$$

$$[W(CO)_3(py)(bipy)] + C_3H_5Cl \xrightarrow{-CO} [WCl(bipy)(CO)_2(\eta^3\text{-}C_3H_5)] + \text{pyridine}$$

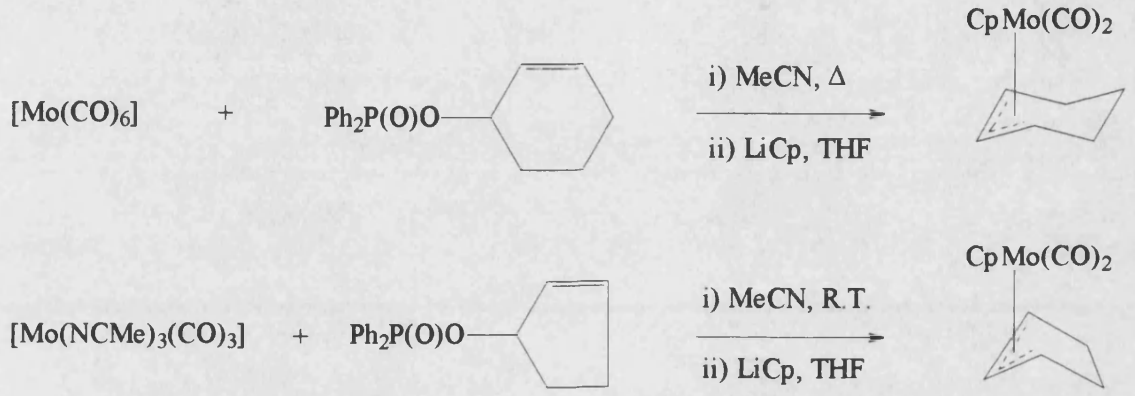


Common features of many of this type of reaction are the displacement of a previously coordinated ligand (*eg* CO), an increase of two in the metal oxidation state and, as the allyl unit formally occupies two coordination sites, an increase in the metal coordination number.

Recently, McCallum *et al* have reported[9] a general method for the synthesis of molybdenum η^3-allyl complexes from the reaction between allylic diphenylphosphinates

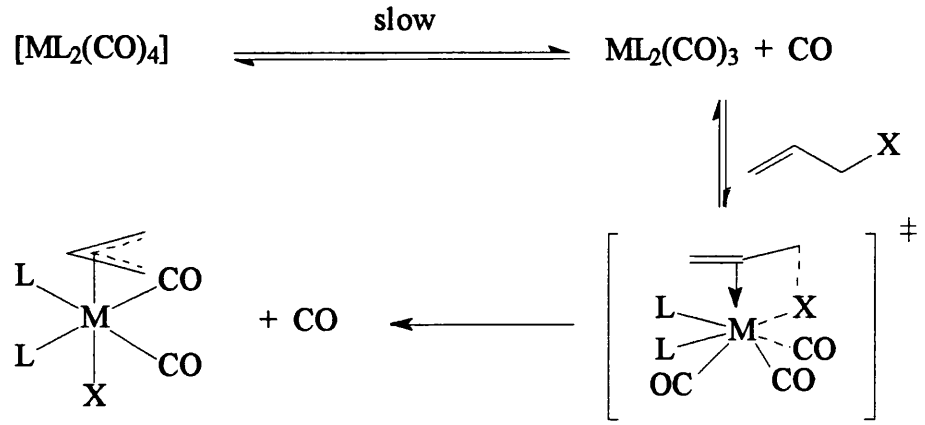
and $[Mo(CO)_6]$ or $[Mo(NCMe)_3(CO)_3]$ followed by treatment with LiCp in THF **(Scheme 2.1.2)**.

Scheme 2.1.2



The mechanism of the oxidative addition of allyl compounds to the tetracarbonyl complexes of Group VIB metals, $[ML_2(CO)_4]$ (M=Cr, Mo, W), is thought to proceed *via* an initial rate determining step involving dissociation of a carbon monoxide ligand. Coordination of the allyl compound to the zerovalent metal is then followed by a further elimination of CO affording the η^3-allyldicarbonyl complex following oxidative addition[10] **(Scheme 2.1.3)**.

Scheme 2.1.3

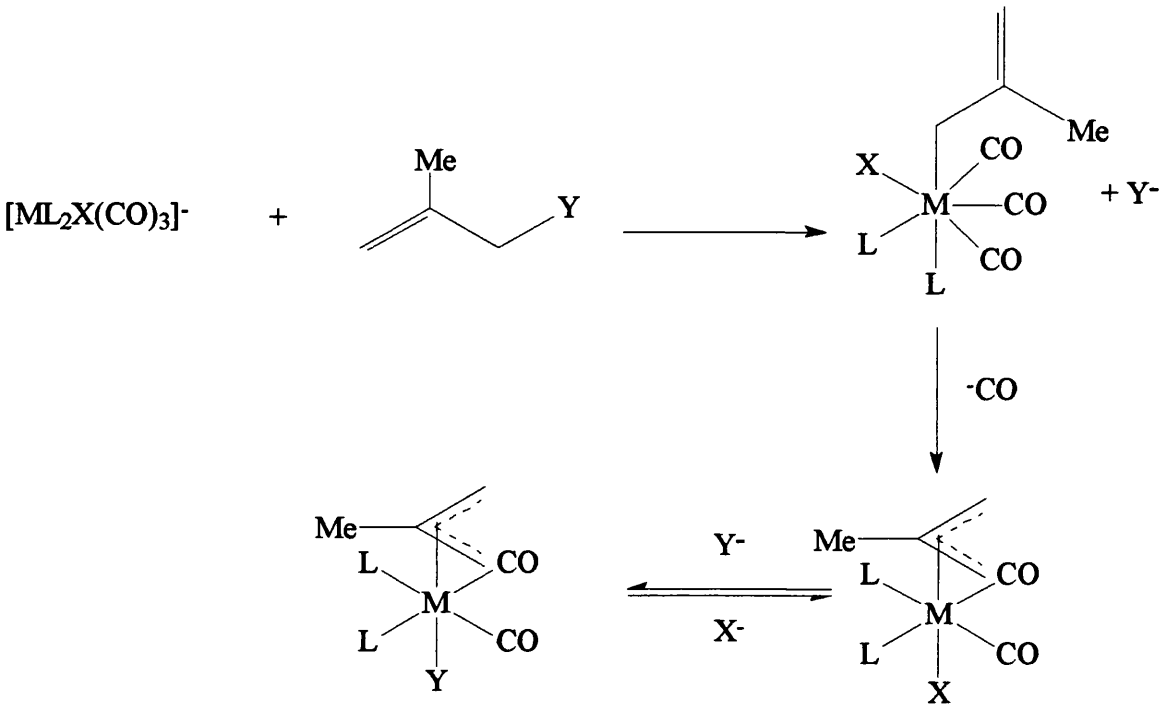


(M=Cr, Mo, W)

The more nucleophilic metal carbonyl anions $[CpMo(CO)_3]^-$ and $[CrCl(bipy)(CO)_3]^-$ also react with, respectively, crotyl bromide and 3-chloro-2-methyl-prop-1-ene to form their corresponding η^3-allyl complexes[6,11,12].

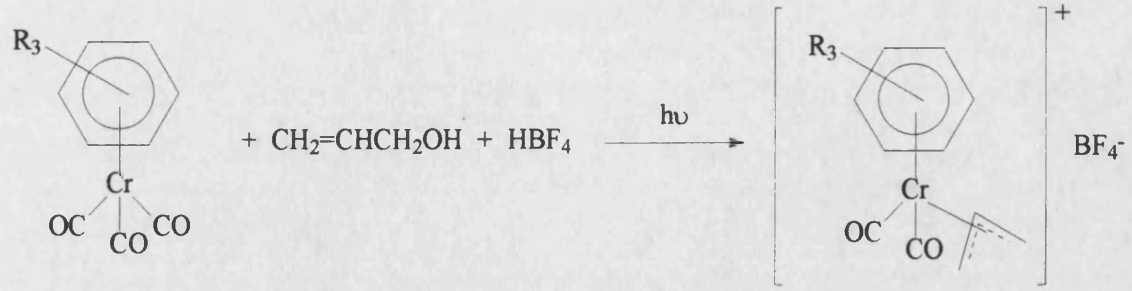
The mechanism for this second reaction, shown in **Scheme 2.1.4**, is thought to involve an initial oxidative addition of the allyl compound *via* an S_N2 type reaction, followed by an $\eta^1 \rightarrow \eta^3$ rearrangement coupled with loss of CO to yield the η^3-allyldicarbonyl complex[11].

Scheme 2.1.4



This reaction provides an important route into the less readily available chromium η^3-allyl complexes[12]. Cationic chromium η^3-allyl complexes can also be prepared *via* the simultaneous action of hydrofluoroboric acid upon a mixture of an arenetricarbonylchromium complex and allyl alcohol[13]. This protonation reaction has also been extended to other metal carbonyls as shown in **Scheme 2.1.5**.

Scheme 2.1.5



R=Me

$$[M(CO)_n] + CH_2{=}CHCH_2OH + HBF_4.Et_2O \xrightarrow{h\upsilon} [M(CO)_{n-1}(\eta^3\text{-}C_3H_5)]^+BF_4^-$$

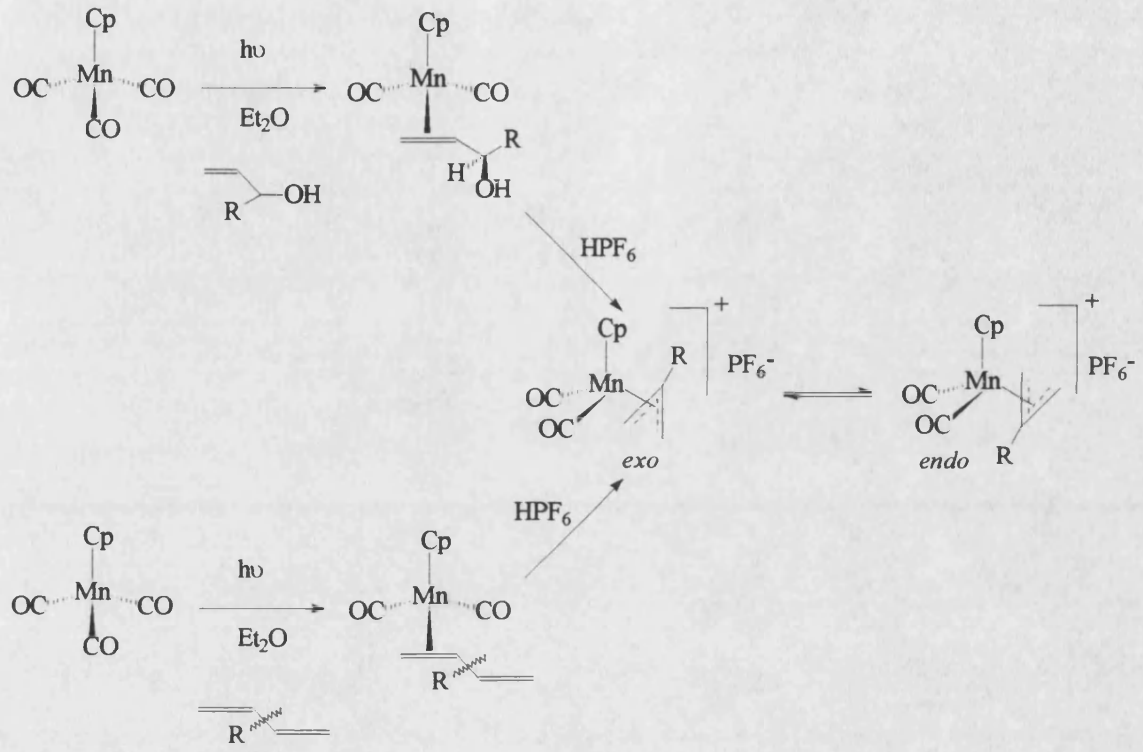
M=Fe; n=5

M=W, Mo; n=6

Alper and subsequently Gibson and his co-workers have employed phase transfer catalysis to prepare η^3-allyl complexes of Co[14] and Fe, Mn and Mo[15]. Alper used a two-phase system of aqueous NaOH/benzene with $PhCH_2NEt^+Cl^-$ as the phase transfer catalyst to synthesise $[Co(CO)_3(\eta^3\text{-}CHR'CR''CH_2)]$ from $[Co_2(CO)_8]$ and allyl halides in high yields[14,16].

The dehydration of allylic alcohols has also been employed by Rosan and Romano in the preparation of cationic manganese η^3-allyl complexes[17]. Similar complexes were also prepared *via* the protonation of coordinated dienes (**Scheme 2.1.6**).

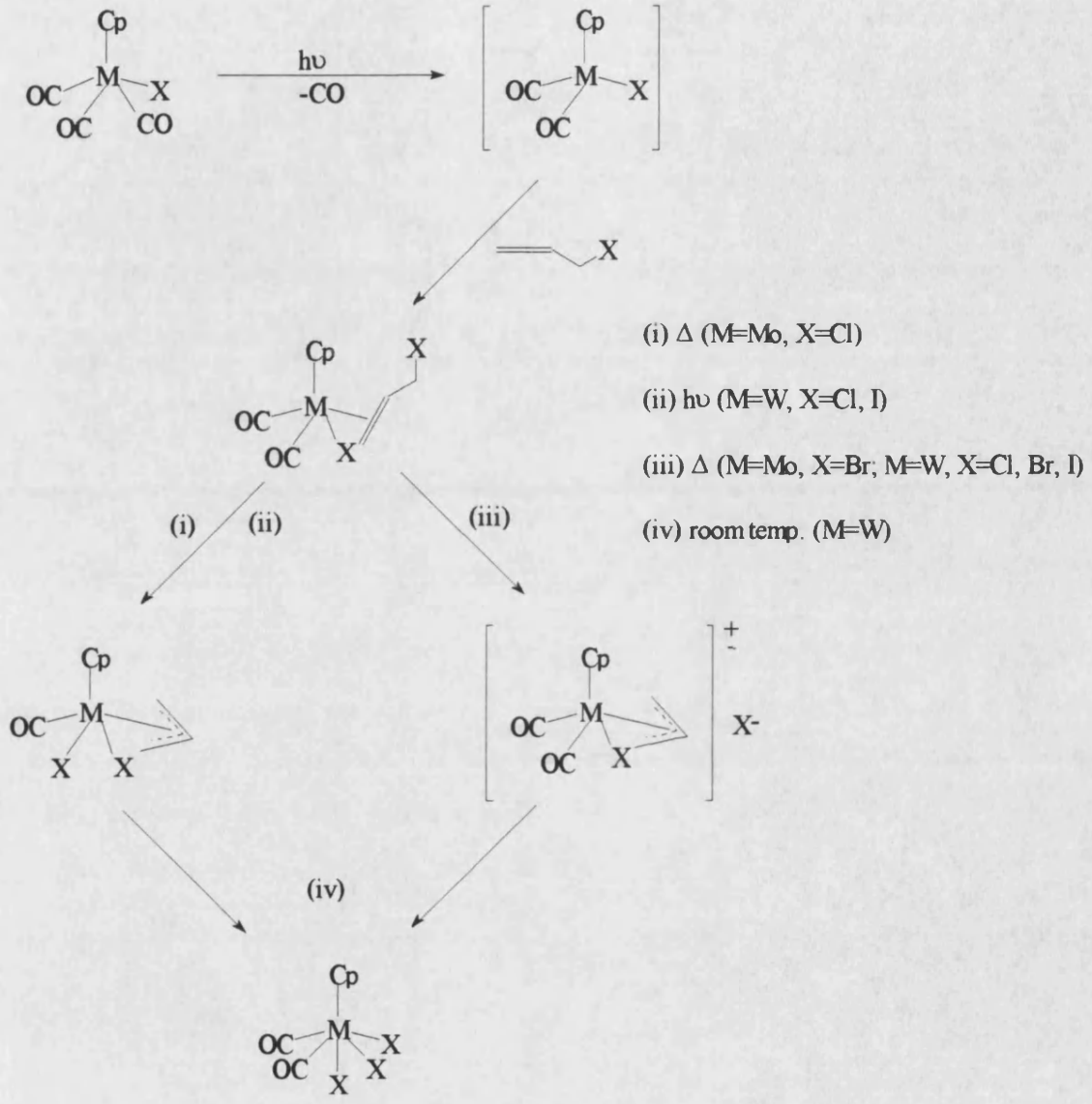
Scheme 2.1.6



R=H, CH_3

Hill *et al*[18] have reported details of the mechanism of the photoreaction between $[CpMX(CO)_3]$ and allylic halides which leads to the corresponding η^3-allyl complexes depicted in **Scheme 2.1.7**.

Scheme 2.1.7


Cp
M
OC
X
CO
hυ
-CO
X
(i) Δ (M=Mo, X=Cl)
(ii) hυ (M=W, X=Cl, I)
(iii) Δ (M=Mo, X=Br; M=W, X=Cl, Br, I)
(iv) room temp. (M=W)
(i)
(ii)
(iii)
X-
(iv)

2.1.2 By reaction of allyl Grignard reagents with transition metal halides

Allyl Grignard reagents[19-22] and, less commonly, allyl-lithium and other main group metal allyls[23-25], react with certain anhydrous metal halides to produce initially an η^1-allyl intermediate which rapidly converts to an η^3-allyl complex. Examples[19,20] are shown in **Scheme 2.1.8** below.

Scheme 2.1.8

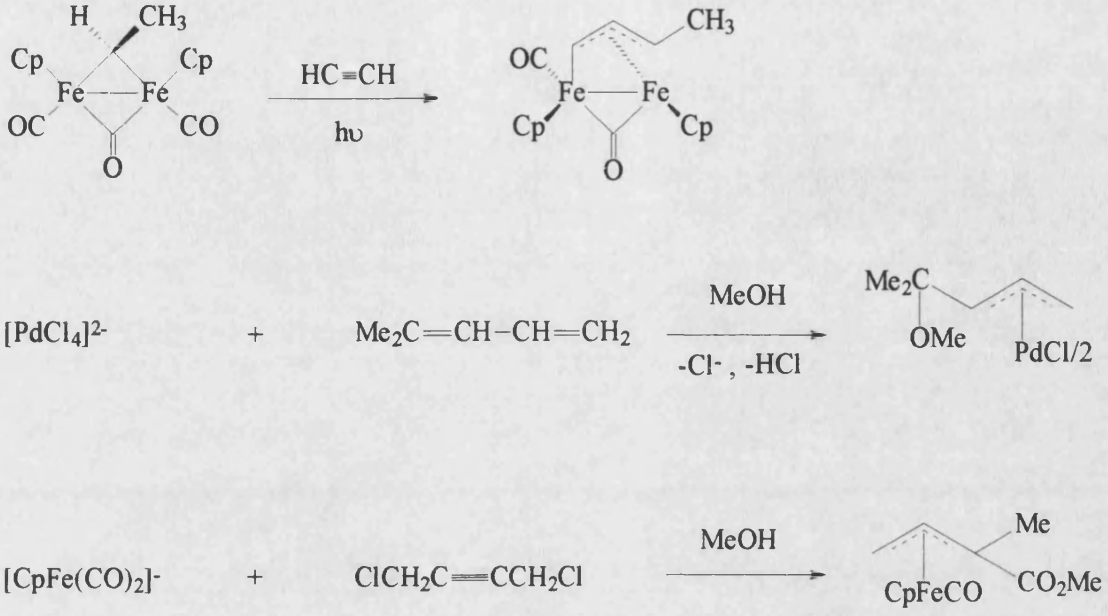
$$[Mo(\eta^6\text{-}C_6H_6)Cl(\eta^3\text{-}C_3H_5)]_2 + 2C_3H_5MgCl \longrightarrow 2MgCl_2 + [Mo(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)_2]$$

$$[Cp_2TiCl] + CH_2{=}CH(CH_2)_2MgCl \xrightarrow{-MgCl_2} [Cp_2Ti(CH_2)_2CH{=}CH_2] \longrightarrow [Cp_2Ti(\eta^3\text{-}1\text{-}MeC_3H_4)]$$

2.1.3 By reaction of 1,3-dienes or alkynes with transition metal complexes

Transition metal η^3-allyl complexes have been successfully prepared *via* the insertion of 1,3-dienes[1] and alkynes[26] into transition metal hydride or alkyl complexes. Metal anions have also been reacted with dienes[27] or alkynes[28] to give η^3-allyl complexes (**Scheme 2.1.9**).

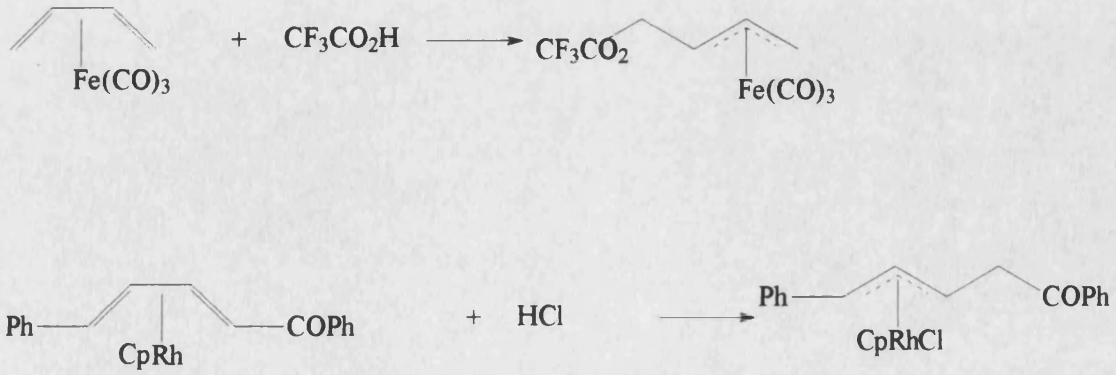
Scheme 2.1.9



2.1.4 By reactions upon coordinated dienes or alkynes

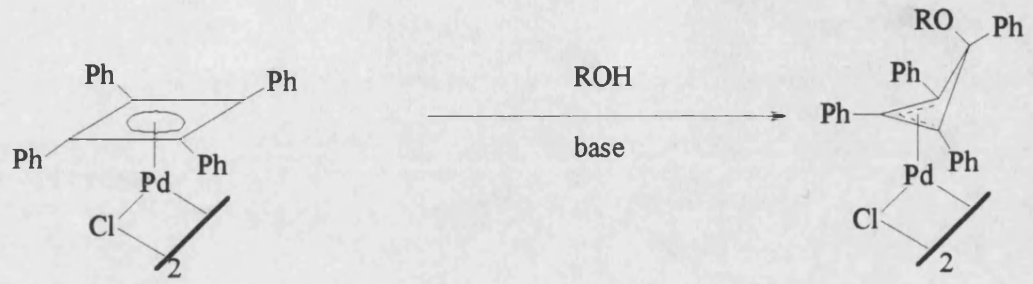
Coordinated 1,3-diene moieties can be protonated directly by acids to give η^3-allyl complexes[29,30] (**Scheme 2.1.10**).

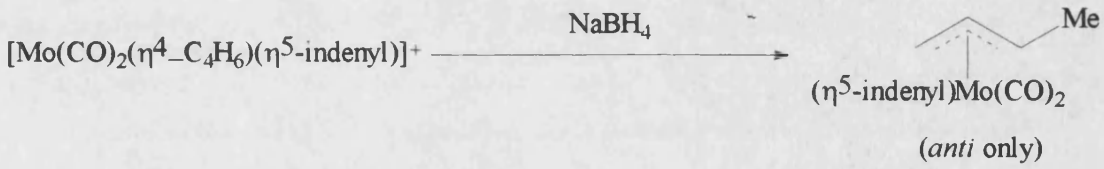
Scheme 2.1.10

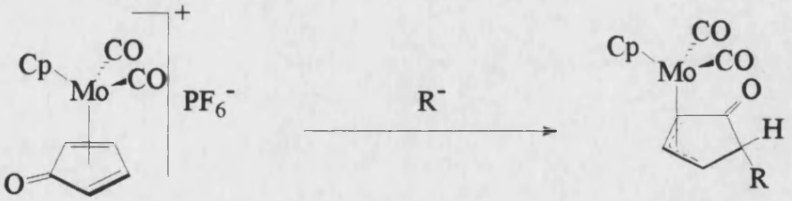


Nucleophilic attack upon a coordinated diene by species such as H^-, OR^- or R^- has also been utilised for the preparation of η^3-allyl complexes[8,31-33] (**Scheme 2.1.11**).

Scheme 2.1.11







R=D, $CH(COOEt)_2$, Me, *n*-Bu, CH_2COPh, $CH{=}CH_2$, *p*-$C_6H_5CH_3$, C≡CPh, 2-oxocyclohexyl

The reaction of alcohols or thiols with molybdenum or tungsten η^1-propargylic complexes also produces a range of η^3-allyl derivatives of these metals[34-37] (**Scheme 2.1.12**).

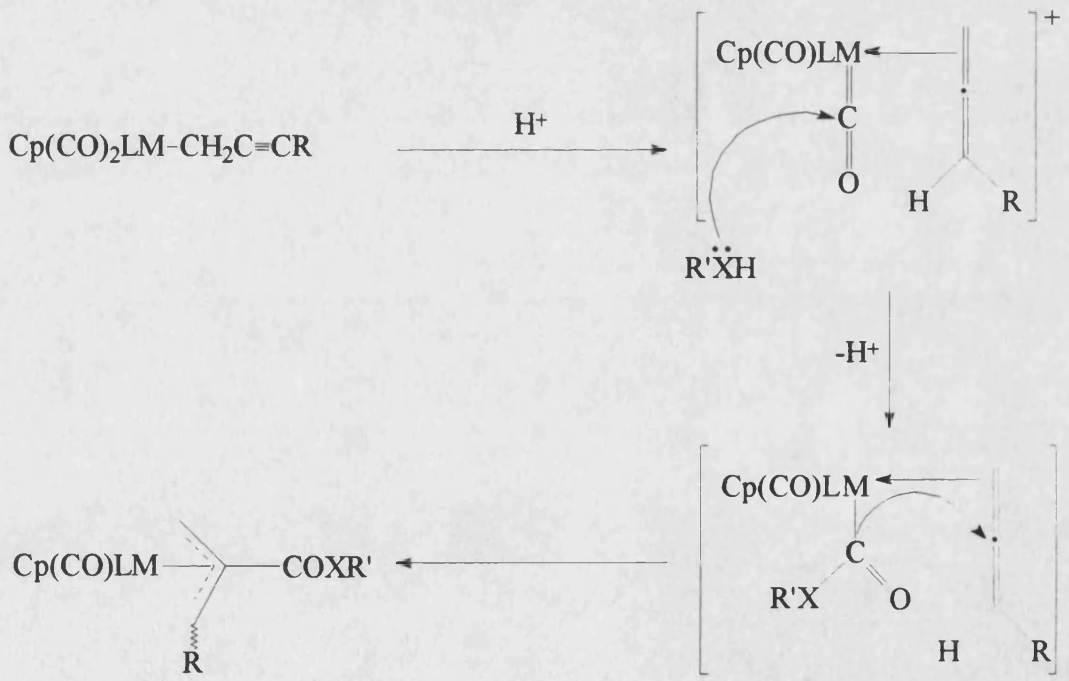
Scheme 2.1.12

$$[\{M\}L(CO)(\eta^1\text{-}CH_2C{\equiv}CR')] + RXH \longrightarrow [\{M\}L\{\eta^3\text{-}1\text{-}R'CHC(COXR)CH_2\}]$$

{M}=M(CO)Cp; M=Mo or W; L=CO, PPh_3, $P(OMe)_3$, $P(OPh)_3$; R, R'=H, alkyl or aryl; X=O or S

These reactions involve alkoxy, hydroxy or thioalkoxycarbonylation of the coordinated organic ligand. A proposed mechanism[35] involving a cationic allene intermediate is shown in **Scheme 2.1.13.**

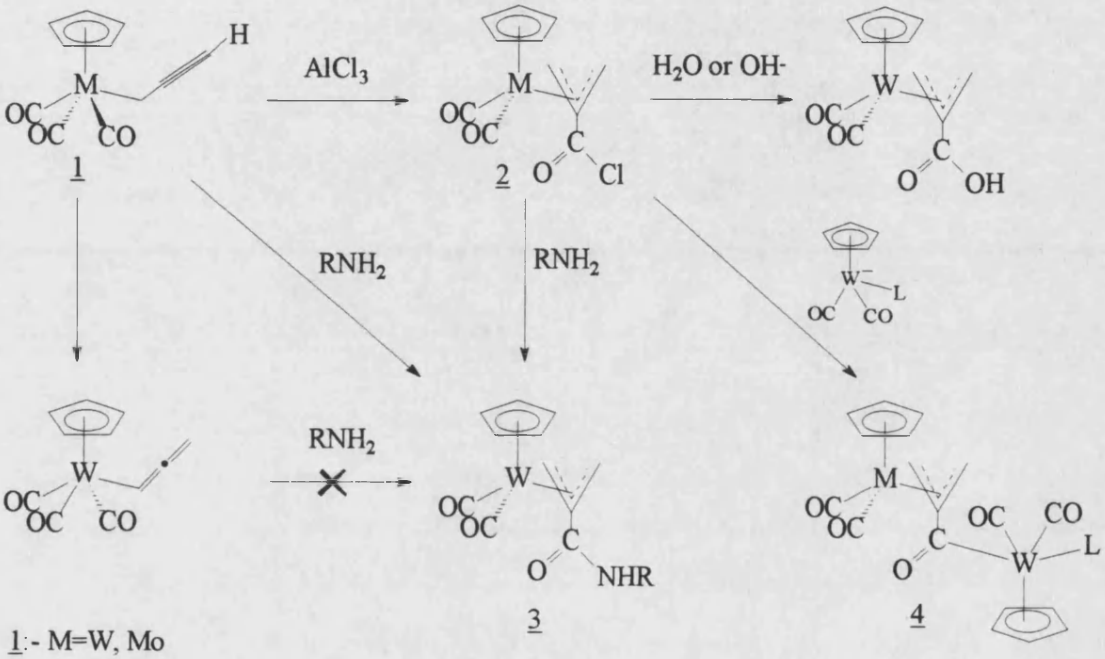
Scheme 2.1.13



Recently, Wu *et al* have prepared molybdenum and tungsten complexes containing (β-chlorocarbonyl)allyl moieties[38]. These complexes react with water or amines to give

the corresponding β-acid or amide substituted allyl derivatives and also with metal anions giving dinuclear complexes in which the two metal atoms are bridged by a four-carbon $\eta^3:\eta^1$ ligand (**Scheme 2.1.14**).

Scheme 2.1.14



1:- M=W, Mo
2:- M=W, Mo
3:- R=Ph, $(CH_2)_2NH_2$
4:- M=W; L=CO, $P(OMe)_3$; M=Mo, L=CO

2.1.5 By conversion of η^1-allyls to η^3-allyl complexes

Chemical[39], thermal[40] and photochemical[41] methods have been used to prepare η^3-allyl complexes from isolable η^1-allyls *via* the loss of two electrons from the metal coordination sphere (**Scheme 2.1.15**). In many reactions, η^1-allyls are frequently postulated as unstable intermediates in η^3-allyl formation.

Scheme 2.1.15

(i) Chemical method (halide extraction)

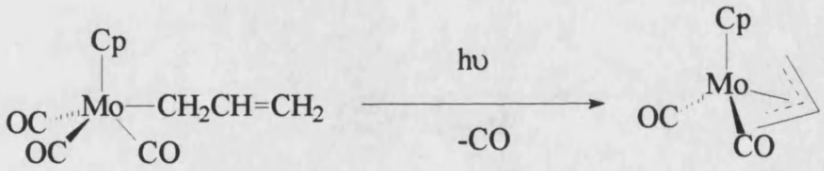
$$Pt(cod)_2 + CH_2{=}CHCH_2Cl \longrightarrow [PtCl(cod)(\eta^1\text{-}C_3H_5)]$$

$$[PtCl(cod)(\eta^1\text{-}C_3H_5)] \xrightarrow{AgBF_4} [Pt(cod)(\eta^3\text{-}C_3H_5)]^+BF_4^- + AgCl$$

(ii) Thermolysis

$$[Mn(CO)_5(\eta^1\text{-}C_3H_5)] \xrightarrow[-CO]{>80^oC} [Mn(CO)_4(\eta^3\text{–}C_3H_5)]$$

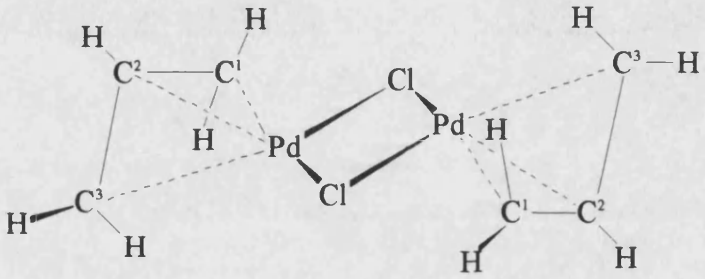
(iii) Photolysis



2.2 Structure and Bonding in η^3-Allyl Complexes

The first η^3-allyl transition metal complex to be characterised by X-ray diffraction[42-45] was the dimer $[PdCl(\eta^3\text{-}C_3H_5)]_2$. The allyl group was found to be bonded symmetrically to the metal with the C-C bond length averaging 1.376(15)Å. The plane containing the allyl ligand was observed to be tilted at an angle of 111.5° ±0.9° to the $PdCl_2Pd$ plane[45] (**Figure 2.2.1**).

Figure 2.2.1:- ***Orientation of the η^3-allyl ligand in $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$***



Subsequently, X-ray diffraction studies on a variety of other η^3-allyl complexes have consistently shown the allyl ligand is not perpendicular to the usual coordination plane of the complex (**Table 2.2.1**).

The reason for this arrangement can be explained by consideration of the bonding interactions between the metal centre and the allyl ligand. Using Hückel calculations[54], the three molecular orbitals Ψ_1, Ψ_2 and Ψ_3 are formed from the allyl carbon atom $2p_z$ orbitals not involved in the σ-bonded framework of the allyl moiety (**Figure 2.2.2**).

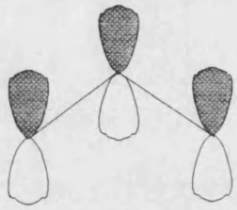
Table 2.2.1	**Dihedral angle**[1]		**Bond lengths**		
Complex	**χ°**	**MC(1)**	**MC(2)**	**MC(3)**	**Ref**
$[Mo(bipy)(py)(CO)_2(\eta^3\text{-}C_3H_5)]$	107.9	2.306(8)	2.279(10)	2.290(9)	46
$[Fe(CO)_3(\eta^3\text{-}C_3H_5)]_2$	98.9	2.208(4)	2.104(4)	2.195(4)	47
$[NiBr(\eta^3\text{-}2\text{-}C_2H_5CO_2C_3H_4)]_2$	106.2	2.050(17)	1.900(21)	2.060(25)	48
$[PdCl(\eta^3\text{-}C_3H_5)]_2$	111.5	2.140(24)	2.020(37)	2.170(28)	44
$[Mo\{P(OMe)_3\}_2Cl(CO)_2(\eta^3\text{-}C_3H_5)]$	112.2	2.403(20)	2.347(24)	2.407(22)	49
$[Ir(PMe_2Ph)_2Cl(CO)(\eta^3\text{-}C_3H_5)]^+$	126.0	2.28(1)	2.24(1)	2.25(1)	50
$[Rh(AsPh_3)Cl_2(\eta^3\text{-}2\text{-}C_3H_4Me)]$	126.6	2.246(16)	2.267(14)	2.226(13)	51
$[Ni(dppe)Br(\eta^3\text{-}2\text{-}C_3H_4Me)]$	106.5	2.059(14)	2.020(14)	2.049(14)	52
$[Cp_2Ti(\eta^3\text{-}1,2\text{-}C_3H_3Me_2)]$	124.1	2.34(3)	2.43(3)	2.35(3)	53

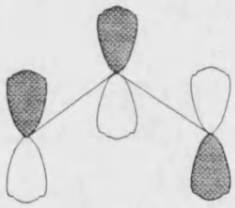
[1] Dihedral angle=angle between the allyl plane and the plane passing through the centre of the allyl, metal and *trans* ligand

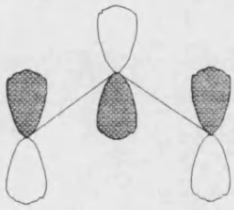
Figure 2.2.2

Atomic Orbitals

ϕ_1 ϕ_2 ϕ_3



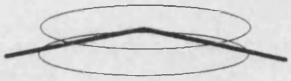




E=Energy
α=Coulomb integral
β=resonance integral

Molecular Orbitals

Ψ_1 Bonding

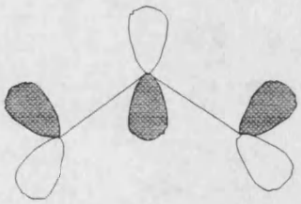


$\Psi_1=1/2\phi_1 + \sqrt{1/2}\phi_2 + 1/2\phi_3$
$E=\alpha + \sqrt{2}\,\beta$

Ψ_2 Non-Bonding

$\Psi_2=\sqrt{1/2}(\phi_1-\phi_3)$
$E=\alpha$

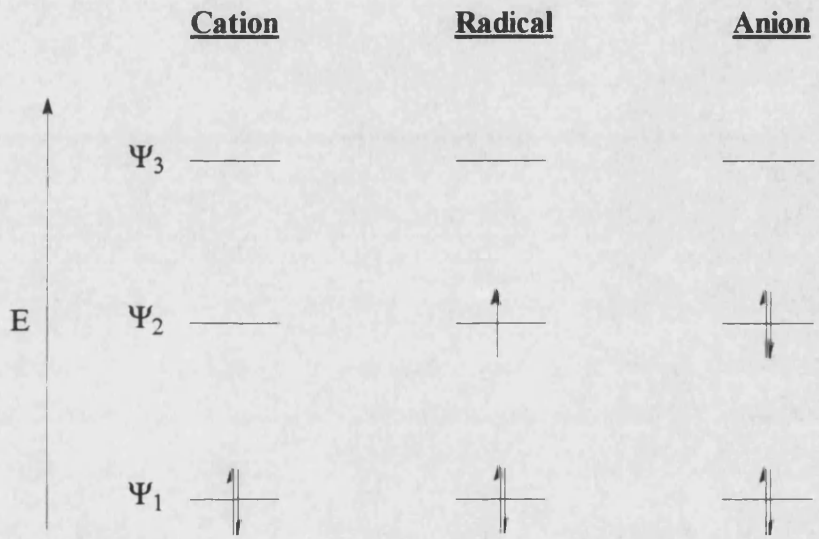
Ψ_3 Anti-Bonding



$\Psi_3=1/2\phi_1 - \sqrt{1/2}\phi_2 + 1/2\phi_3$
$E=\alpha - \sqrt{2}\,\beta$

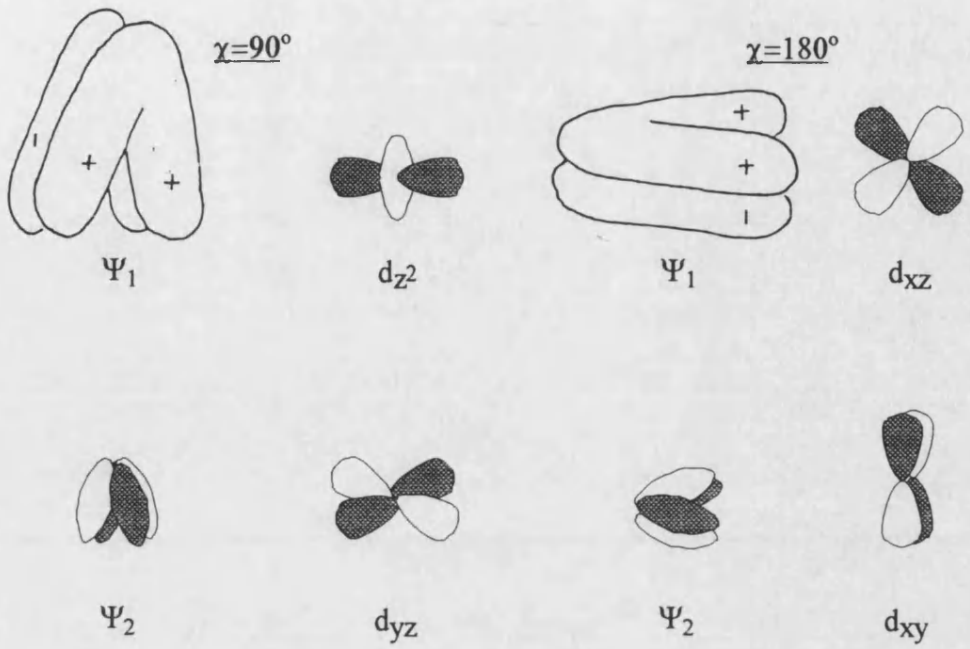
In order to accommodate the number of electrons donated by the allyl moiety, which can be considered as a cationic two electron, neutral three electron or anionic four electron donor ligand, changes in the formal oxidation state of the metal can be made; however the allyl group is usually considered to be an anionic four electron donor ligand, thus contributing one unit to the valency of the metal (**Figure 2.2.3**).

Figure 2.2.3



To explain the observed tilt of the allyl plane with respect to the $PdCl_2Pd$ plane, Kettle and Mason[55] developed a bonding scheme for $[PdCl(\eta^3\text{-}C_3H_5)]_2$ which proposed two possible overlap mechanisms with χ=90° or χ=180° as shown in **Figure 2.2.4**.

Figure 2.2.4



From M.O. calculations, the Ψ_1- and Ψ_2-metal bonding interactions are maximised at dihedral angles (χ) of 114° and 102° respectively. As energy considerations indicate the Ψ_1 orbital to play the major role in the palladium-allyl bonding, a dihedral angle of 114°, in close agreement with the observed angle of 111.5°, is thus favoured.

Subsequently however, van Leeuwen and Praat[56] came to the conclusion that the interaction of the allyl Ψ_2 and metal $d_{(x^2-y^2)}$ orbitals provides the most important contribution to the metal-allyl bonding in $[PdCl(\eta^3\text{-}C_3H_5)]_2$. The most favourable configuration is shown in **Figure 2.2.5A**. The two carbon atoms are in the plane of the metal ion and ligands A and B (*ie* Cl in this case). The allyl unit can thus be seen to act as a bidentate ligand. **Figure 2.2.5B** shows a configuration in which back-donation from filled metal orbitals to the empty Ψ_3 can occur. The Ψ_3 orbital has a nodal plane perpendicular to the allyl plane intersecting the two carbon-carbon bonds. Thus maximum overlap of Ψ_3 with Pd-p_z and a combination of $Pd(d_{xz}+d_{yz})$ occurs when the allyl nodal

plane coincides with the metal nodal plane (xy), as in **Figure 2.2.5B** in which the two terminal carbon atoms are placed below the xy-plane.

As the configuration in **Figure 2.2.5B** would cause a significant decrease in the most important bonding combination, that in **Figure 2.2.5A**, the allyl ligand must tilt in such a way that the p-orbitals of the terminal carbon atoms give a good interaction with the metal ($d_{x^2-y^2}$) orbital and the nodal (xy) plane still approximately intersects the two nodes of Ψ_3 (**Figure 2.2.5C**). The central carbon atom is now closer to the metal ion thus also enlarging the interaction of Ψ_1 with the empty metal orbitals. More recent calculations[57] have refined, but not essentially changed these conclusions.

Figure 2.2.5A:- $\Psi_2 + d_{(x^2-y^2)}$

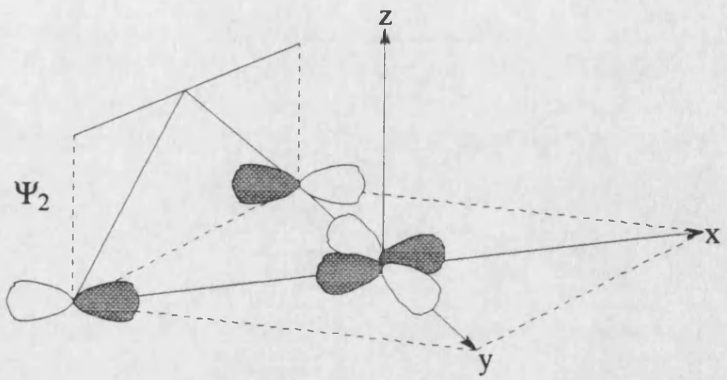


Figure 2.2.5B:- $\Psi_3 + d_{(xy/yz)} + p_z$

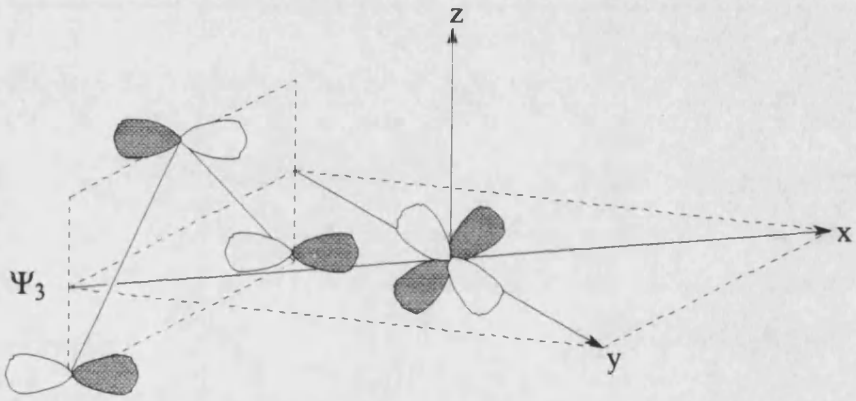
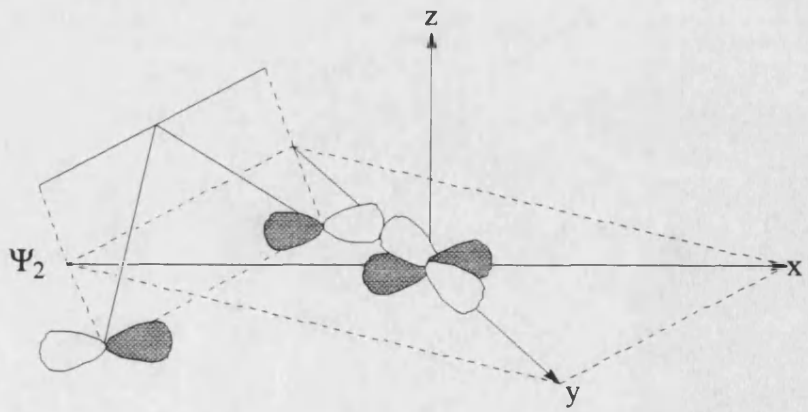


Figure 2.2.5C:- $\Psi_2 + d_{(x^2-y^2)}$

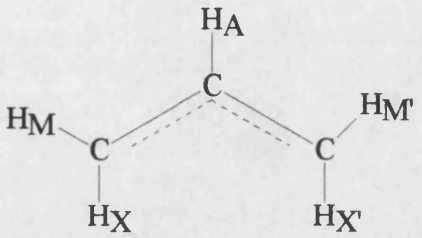


2.3 Spectroscopic Characterisation of η^3-Allyl Complexes

2.3.1 ^{1}H NMR spectroscopy

Theoretically an η^3-C_3H_5 containing complex of low symmetry could have up to five magnetically non-equivalent protons. However there are three groups of magnetically distinct protons H_A, H_M and H_X present for an η^3-C_3H_5 group in a symmetrical environment. Although an AMM'XX' spin pattern would be expected for this type of system, an AM_2X_2 spin system is usually observed as the coupling constants J_{MX}, $J_{M'X'}$ and $J_{MX'}$, $J_{M'X}$ are small and are rarely detected. The small J_{MX} and $J_{M'X}$ values are due to the angle between H_M and H_X being approximately 120° (consistent with sp^2 hybridisation of the carbon atom), whilst $J_{MX'}$ and $J_{M'X}$ arise from long range coupling. Values for $J_{MM'}$ and $J_{XX'}$ are similarly small due to the large separation between H_M and $H_{M'}$ and H_X and $H_{X'}$. Typical chemical shift values and coupling constants are shown in **Figure 2.3.1**.

Figure 2.3.1



H_M and $H_{M'}$ = H_{syn}

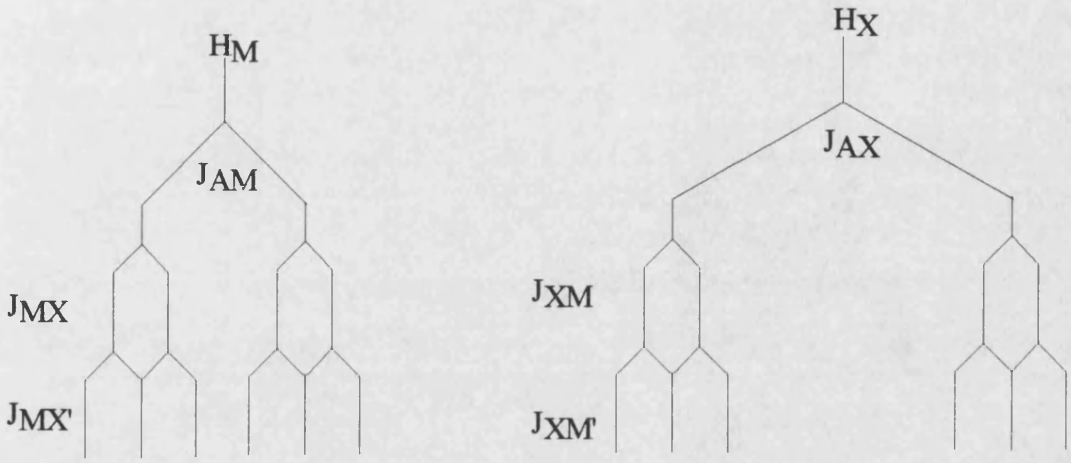
H_X and $H_{X'}$ = H_{anti}

Typical values	H_A	H_M	H_X
Chemical shift (δ)	6.5-4ppm	5-2.5ppm	4-1ppm
Coupling constants (J)		5-10Hz	9-14Hz

As the *trans*-coupling constant (J_{AX}) is greater than the *cis*-coupling constant (J_{AM}) the higher field doublet is assigned to the *anti*-protons (H_X) which are shielded by the metal to a greater extent than the *syn*-protons (H_M) and would therefore be expected to resonate at a higher field.

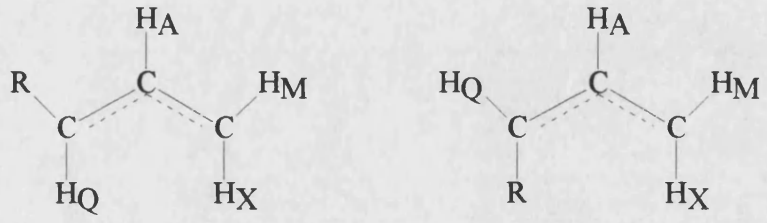
A high resolution study[58] of $[Pd_2I_2(\eta^3\text{-}C_3H_5)_2]$ has successfully resolved fifteen of the sixteen "lines" expected for the central allylic hydrogen (*ie* H_A) in an AMM'XX' type spin system. The two doublets manifested by the *syn*- and *anti*-protons (H_M and H_X respectively) were resolved as triplets caused by J_{MX} and $J_{MX'}$ apparently having equivalent values of approximately 1Hz (**Figure 2.3.2**).

Figure 2.3.2



Substitution at the central carbon of H_A for another group generally leads to simplified spectra, however substitution at the 1-position of H_M or H_X leads to *syn*- and *anti*-isomerism[59-61] and thus more complex spectra (**Figure 2.3.3**).

Figure 2.3.3



syn *anti*

The *syn*- and *anti*-isomers can be differentiated between by the higher *trans*-coupling constant (J_{AQ}) exhibited by the *syn*-isomer.

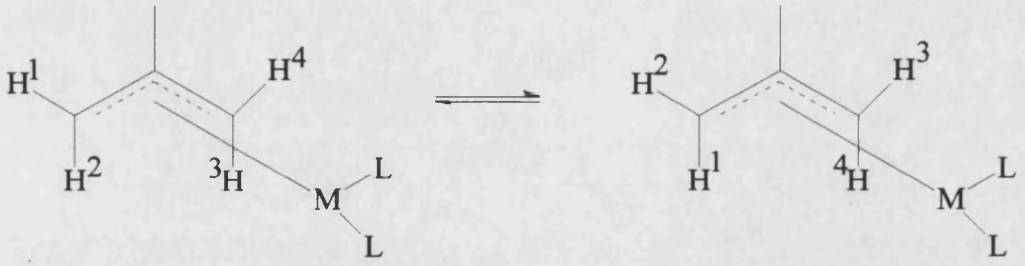
2.3.2 Fluxional allyl complexes

Stereochemically non-rigid or fluxional η^3-allyl complexes are common[62]. These dynamic complexes can often give deceptively simple ^1H NMR spectra due to rearrangements at or just above room temperature. The rearrangements may occur by motion of the η^3-allyl group alone with respect to the rest of the complex, or alternatively by movement of other ligands about the metal centre as noted above. The precise mechanisms of these rearrangements are not completely defined in all cases however the following have been commonly observed.

(a) *Syn-anti* exchange

The overall result of this process is rapid interchange of the *syn*- and *anti*-protons of the allyl system as shown in **Scheme 2.3.1**.

Scheme 2.3.1

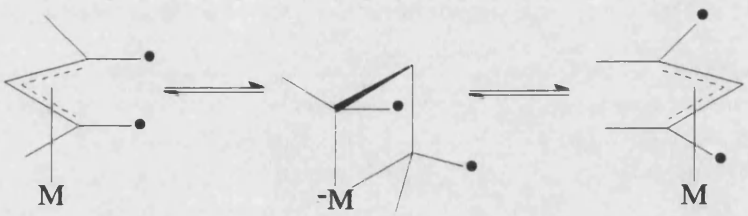


The most generally accepted mechanism for this rearrangement is an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ interchange[63] which has been proved to occur in the complexes $[Pd(P)Cl(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)]$ ($P=PPhMe_2$, R=methyl; $P=PPh_3$, R=isopropyl). Other less probable mechanisms such as a flip of the allyl group *via* a σ-σ bonded allyl system and the rapid rotation of a CH_2 group

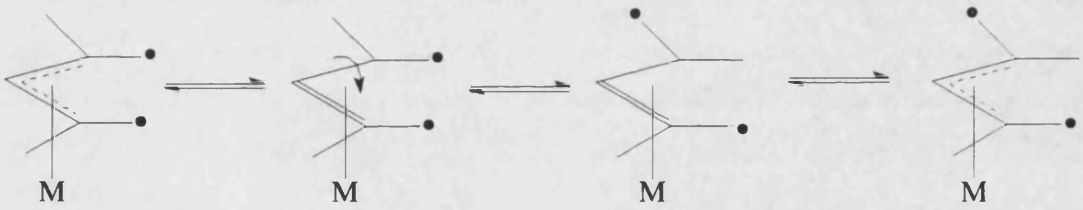
about a carbon-carbon single bond of an η^2-allyl intermediate have also been proposed. These mechanisms are depicted in **Scheme 2.3.2**.

Scheme 2.3.2

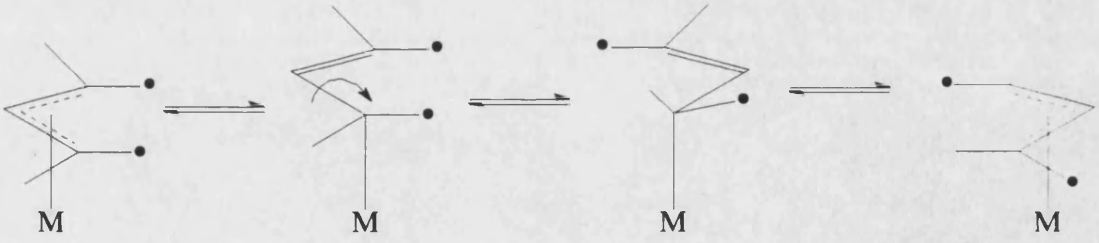
(i)



(ii)



(iii)



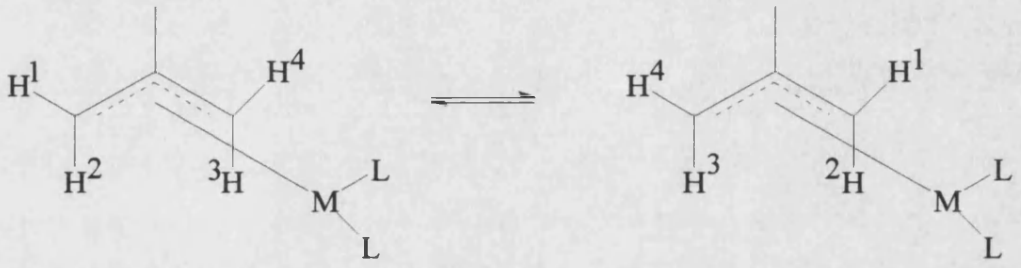
Syn-anti exchange results in AX_4 type spin systems in which the terminal hydrogens of the allyl ligand appear to be magnetically equivalent. At low temperatures

the homoleptic complexes [M(η^3-C_3H_5)$_4$] (M=Zr, Ti) have been observed[64-66] to revert to the normal AM_2X_2 spin systems.

(b) *Syn,syn-anti,anti exchange*

This rearrangement can be considered to be an interchange of *syn,syn* and *anti,anti*-protons as shown in **Scheme 2.3.3.**

Scheme 2.3.3

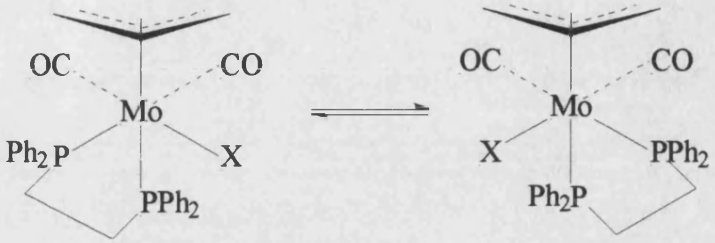


The exchange can be detected easily by ^1H or ^{13}C NMR spectroscopy studies on low symmetry complexes containing the η^3-C_3H_5 group; an AGMPX spin pattern is observed at low temperatures in ^1H NMR spectra, which simplifies to an AM_2X_2 pattern at higher temperatures *ie* the *syn,syn* and *anti,anti* protons become equivalent. The observed time-averaged environment for the terminal allylic protons can be envisaged as the result of either a rotation of the allyl moiety about the metal-allyl axis or by *pseudo*rotation of other ligands about the metal centre.

Variable-temperature ^1H, ^{13}C and ^{31}P NMR studies of [MoX(diphos)(CO)$_2$(η^3-C_3H_5)] (X=halide) led Faller *et al*[67] to propose a "trigonal twist" rearrangement (*ie* *pseudo*rotation of the triangular face containing the halide and two phosphorus atoms)

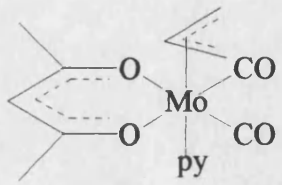
rather than a rotation of the allyl group to explain the observed equivalence of the terminal allyl protons above low temperatures (**Scheme 2.3.4**).

Scheme 2.3.4

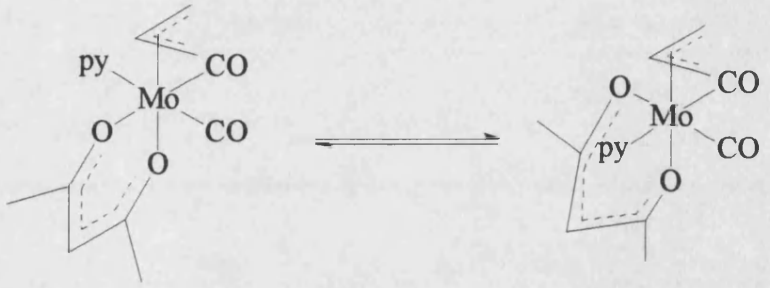


Variable temperature ^{1}H and ^{13}C NMR spectra obtained in $CDCl_3$ for the complex $[Mo(pda)(py)(CO)_2(\eta^3\text{-}C_3H_5)]$ were reported by Brisdon and Woolf[68] to show the co-existence of two isomers at low temperature in a ratio (**(a)**:**(b)**) of 1.6:1. Isomer **(a)** (as shown in **Scheme 2.3.5** below) had a spin pattern for the allyl ligand of the AM_2X_2 type whereas isomer **(b)** exhibited an AGMPX spin pattern. At elevated temperatures isomer **(b)** undergoes a *pseudo*-trigonal twist resulting in a simplified ^{1}H NMR spectrum containing an AM_2X_2 spin pattern. Although isomer **(a)** is temperature invariant at this point, higher temperatures lead to a rapid interconversion of the two isomers with the two AM_2X_2 spin patterns collapsing to a single AM_2X_2 pattern. This suggests that the ligand face formed by the pyridine and pda ligands undergoes a complete rotation at more elevated temperatures.

Scheme 2.3.5



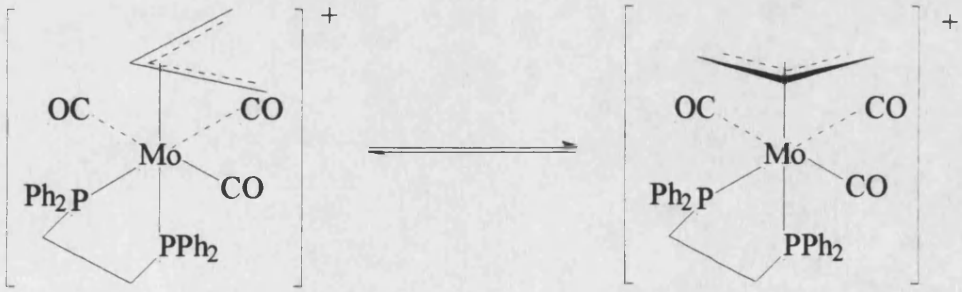
(a)



(b)

In contrast the *syn,syn, anti, anti* exchange observed in the ^1H NMR spectrum of the cationic molybdenum complex $[Mo(diphos)(CO)_3(\eta^3\text{-}C_3H_5)][PF_6]$ has been explained[69] by a restricted rotation about the allyl-metal bond of 90° clockwise or 270° anti-clockwise by the allyl ligand (**Scheme 2.3.6**).

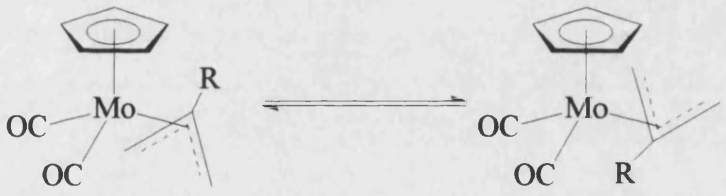
Scheme 2.3.6



(c) Conformational isomerism

Conformational isomerism results through restricted rotation of the η^3-allyl group about the metal-allyl axis in complexes such as $[CpMo(CO)_2(\eta^3\text{-}2\text{-}C_3H_4R)]$ (R=H, Me)[70,71]. With R=H, the exo/endo conformer ratio K(exo/endo)=4.7 but when R=Me, K(exo/endo)=0.38, indicating that steric interactions between the cyclopentadienyl ring and the allyl ligand provide a barrier to interconversion. The two overlapping AM_2X_2 spin patterns observed in the ^1H NMR of the complexes below (**Scheme 2.3.7**) at 5°C collapse at higher temperatures to a single AM_2X_2 pattern due to the rotation of the allyl ligand becoming fast on the NMR time scale[70].

Scheme 2.3.7

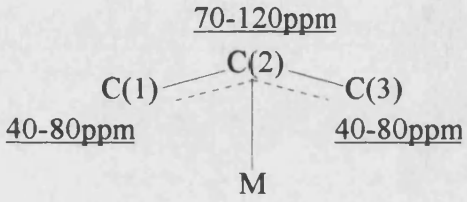


exo endo

2.3.3 ^{13}C NMR spectroscopy[72]

The ^{13}C NMR shift values for η^3-allyl ligands are generally found within the characteristic ranges shown in **Figure 2.3.4**. Thus, for unsubstituted η^3-allyl complexes, the terminal carbons C(1) and C(3) are generally found between 40-80ppm, the central carbon C(2) is found at lower field, typically between 70-120ppm. Methyl substitution causes deshielding with a consequent downfield shift compared to the unsubstituted analogue.

Figure 2.3.4



Typical J(^{13}C-^{13}C) and J(^{13}C-^{1}H) coupling constants are 40-50 and 155-180Hz respectively. **Table 2.3.1** overleaf lists ^{13}C chemical shifts and, where available, J(^{13}C-^{13}C) and J(^{13}C-^{1}H) coupling constants for some relevant complexes.

Dynamic η^3-allyl species have also been examined by variable temperature ^{13}C NMR spectroscopy, for example the conformational isomerism observed in the complex [Rh(η^3-C_3H_5)$_3$] is believed[75,76], on the basis of ^{1}H NMR evidence, to arise from the rotation of *one* allyl group in its own plane as shown in **Scheme 2.3.1**. Support for this comes from the presence at -75°C in the complex's ^{13}C NMR spectrum of three signals for both the terminal and central carbons of the allyl groups. Higher temperatures result in

two sharp and four broad signals and at room temperature the latter coalesce into two sharp peaks[76].

Scheme 2.3.8

Table 2.3.1

Complex	Chemical Shift δ (ppm)[1] C(1)	C(2)	C(3)	Coupling constant, J(Hz)	Ref.
$[MoCl(dppe)(CO)_2(\eta^3\text{-}C_3H_5)]$	60.4	83.7	60.4		67
$[WCl(dppe)(CO)_2(\eta^3\text{-}C_3H_5)]$	52.2	73.0	52.2		67
$[Pd(acac)(\eta^3\text{-}1\text{-}C_3H_4R)]$ (R=H)	55.8	113.5	55.8		58
$[Pd(acac)(\eta^3\text{-}1\text{-}C_3H_4R)]$ (R=Me)	73.6	113.3	51.6		58
$[Pd(acac)(\eta^3\text{-}1\text{-}C_3H_4R)]$ ($R=CH_2Ph$)	77.6	112.0	52.6		58
$[Mo(bipy)\{P(OPh)_3\}(CO)_2(\eta^3\text{-}2\text{-}C_3H_4Me)]^+$	64.1	94.9	64.1	J[P-C(2)]=7	73
$[Mo(bipy)(py)(CO)_2(\eta^3\text{-}2\text{-}C_3H_4Me)]^+$	58.8	86.2	58.8		73
$[Mn(CO)_4(\eta^3\text{-}C_3H_5)]$[2]	43.2	93.8	43.8	J[H-C(1)]=J[H-C(3)=161; J[H-C(2)]=157	74

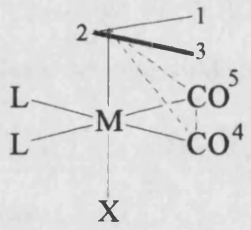
1-determined at room temperature unless noted; **2**-determined at -95°C

C(1) and C(3) refer to the terminal carbon atoms and C(2) to the central carbon atom of the η^3-allyl moiety

2.4 *Pseudo*octahedral η^3-allyldicarbonyl complexes of Group VI transition metals

Crystal structure determinations[46,67,68,77-82] carried out on complexes of the type $[MXL_2(CO)_2(\eta^3\text{-allyl})]^{n\pm,0}$ have shown that virtually all such complexes adopt a *pseudo*octahedral configuration with respect to the metal centre with the η^3-allyl and *cis*-dicarbonyl ligands in a *fac*-arrangement (**Figure 2.4.1**).

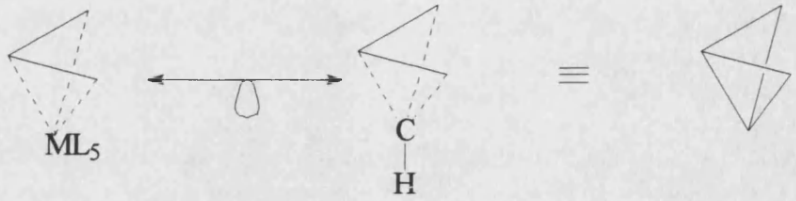
Figure 2.4.1:-*The* fac-*arrangement of the allyl and CO ligands*



In all but one case[83], the open face of the η^3-allyl ligand has been shown to point towards the *cis*-dicarbonyl groups. This rotational preference has been rationalised in terms of the strong d_π-π^*_{CO} back -bonding to the *cis*-dicarbonyl ligands[84,85].

Using the isolobal theories developed by Hoffmann *et al*[86], a d^4 ML_5 fragment ($M=Mo^{II}$) can be considered to be isolobal with CH^+. Thus the ML_5 (η^3-C_3H_5) group is isolobal with (CH^+)($C_3H_5^-$) or bicyclobutane as shown in **Scheme 2.4.1**[84].

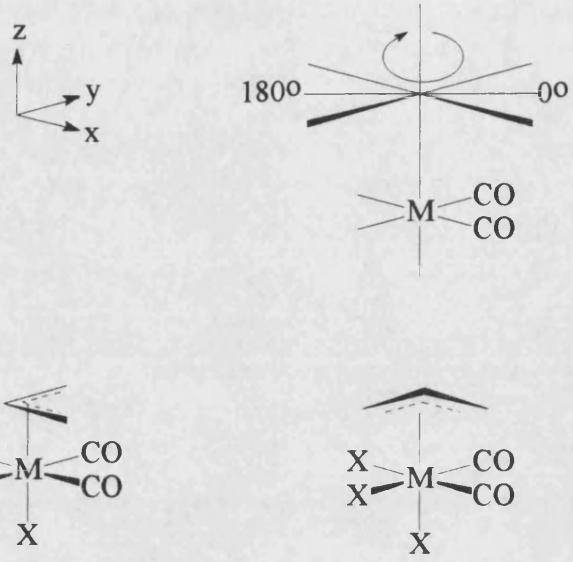
Scheme 2.4.1



There should be no appreciable energy barrier to rotation of the C_3H_5 fragment about the isolobal C-H group and so only a relatively small, second-order effect is expected (and found) to be responsible for the rotational preference of the η^3-C_3H_5 group in $[Mo^{II}L_2X(CO)_2(\eta^3\text{-}C_3H_5)]$ complexes.

FMO analyses made on the model complexes $[MoCl_3(CO)_3(\eta^3\text{-}C_3H_5)]$ and $[Mo(NCH)_3(CO)_2(\eta^3\text{-}C_3H_5)]$ (which were assumed to have perfect octahedral symmetry and a planar allyl ligand parallel to the plane containing the two carbonyl and two X ligands), for three orientations of the allyl ligand (θ=0.0°, 90° or 180°) showed that the θ=0.0° rotamer is the most stable of the three rotamers by about 40-65 kJ mol^{-1} compared to the θ=180° conformation (**Figure 2.4.2**).

Figure 2.4.2

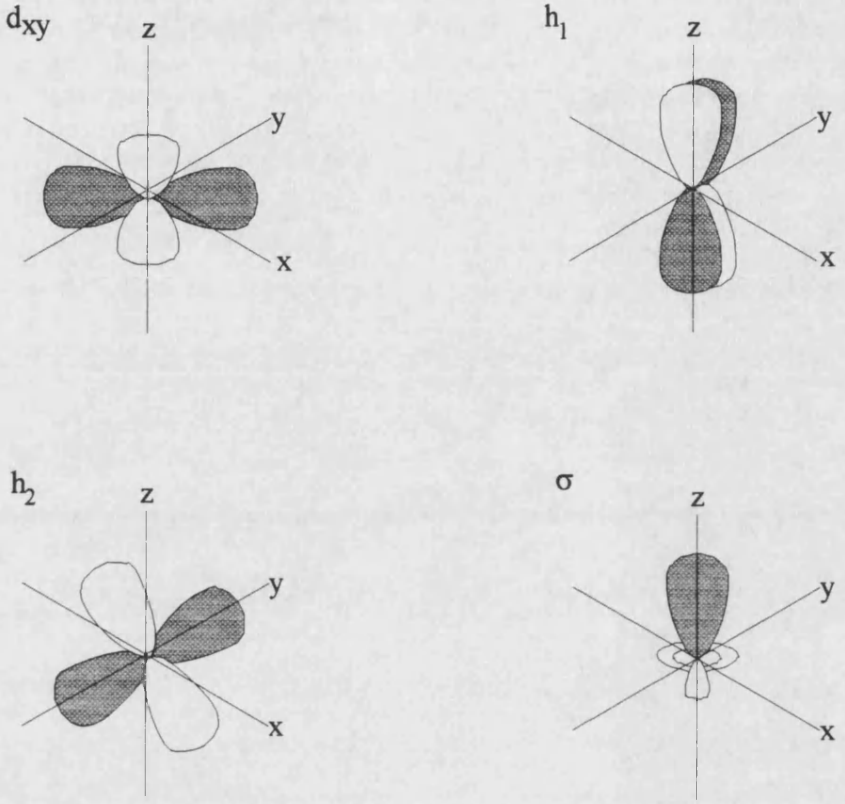


X	θ=0°	θ=90°	θ=180°
HCN	E=0.0	25.6	61.4kJ mol^{-1}
Cl	E=0.0	31.9	42.2kJmol^{-1}

As θ=0° and θ=180° are respectively the lowest and highest energy conformations, only these two extremes will be discussed further.

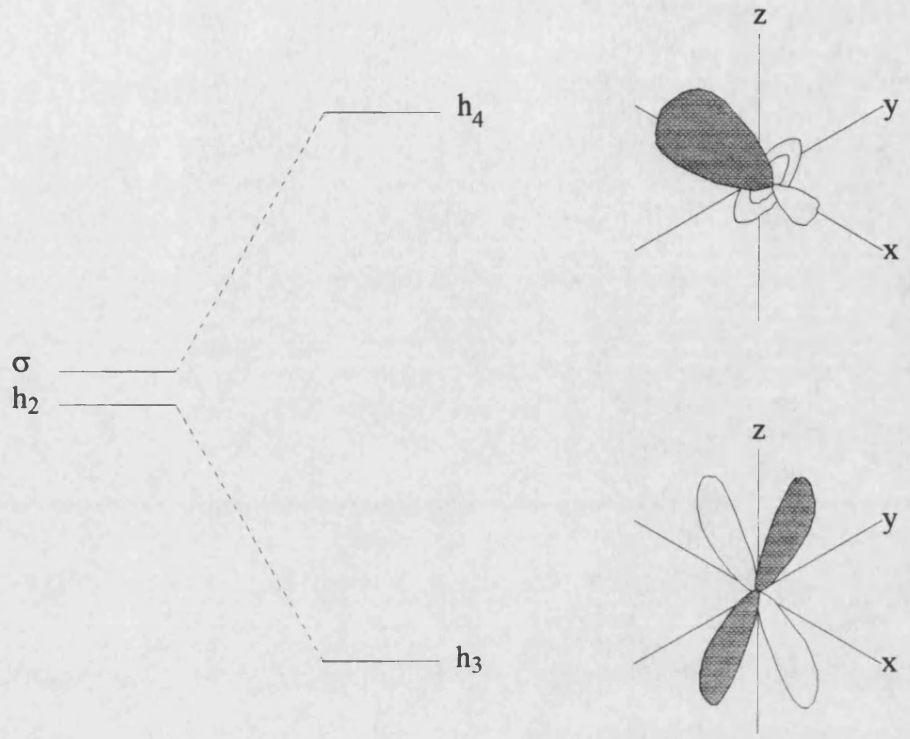
The relevant fragment orbitals are Ψ_1, Ψ_2 and Ψ_3 of the allyl ligand and the frontier orbitals of the ML_5-type fragment. These are made up of the δ-type d_{xy}, which interacts only weakly with the allyl FMO's and hence can be ignored, two nearly degenerate π-type hybrids h_1(=xz-yz) and h_2(≈xz+yz) and a σ-type hybrid composed mainly of d_z2 at higher energies (**Figure 2.4.3**).

Figure 2.4.3:- ***Fragment orbitals of $[MoX_3(CO)_2]$***



Two new hybrid orbitals, h_3 and h_4 are formed by mixing of $h_2(\approx xz+yz)$ and the σ-type hybrid; h_3 and h_4 are tilted toward the central carbon of the allyl group when $\theta=0°$ (**Figure 2.4.4**).

Figure 2.4.4:- ***Mixing of σ and h_2***



However, direct overlap of the σ-symmetry d_z2 hybrid and the π-symmetry h_2 cannot occur in a first-order fashion and mixing is instead achieved *via* interaction with the carbonyl π^* orbitals (**Figure 2.4.5**).

Figure 2.4.5

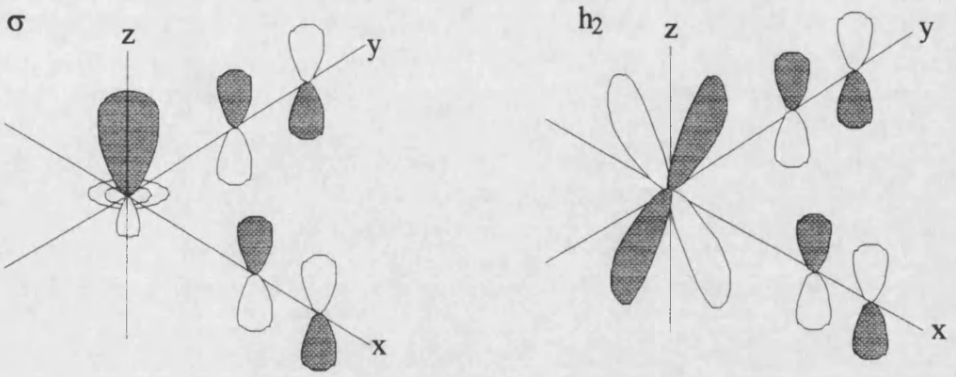


Figure 2.4.6 shows a qualitative M.O. scheme for the interaction of the allyl Ψ_1, Ψ_2 and Ψ_3 orbitals with the $[MoX_3(CO)_2]$ fragment orbitals. As shown below, the tilted hybrid orbital h_3 is destabilised on interaction with the filled Ψ_1 molecular orbital. This interaction is greater for the $\theta=180°$ rotamer as the central carbon atom of the allyl ligand points towards the dicarbonyl group in this conformation. Thus, the rotational preference of the allyl ligand can be explained by the fact that the HOMO of the complex *will be destabilised more* when $\theta=180°$ than when $\theta=0°$ (*nb* the remaining orbitals of the complex were shown to exhibit little variation in energy as the allyl ligand is rotated). **Figure 2.4.7** summarises the interactions of h_1 and h_3 for $\theta=0°$ and $\theta=180°$.

Figure 2.4.6

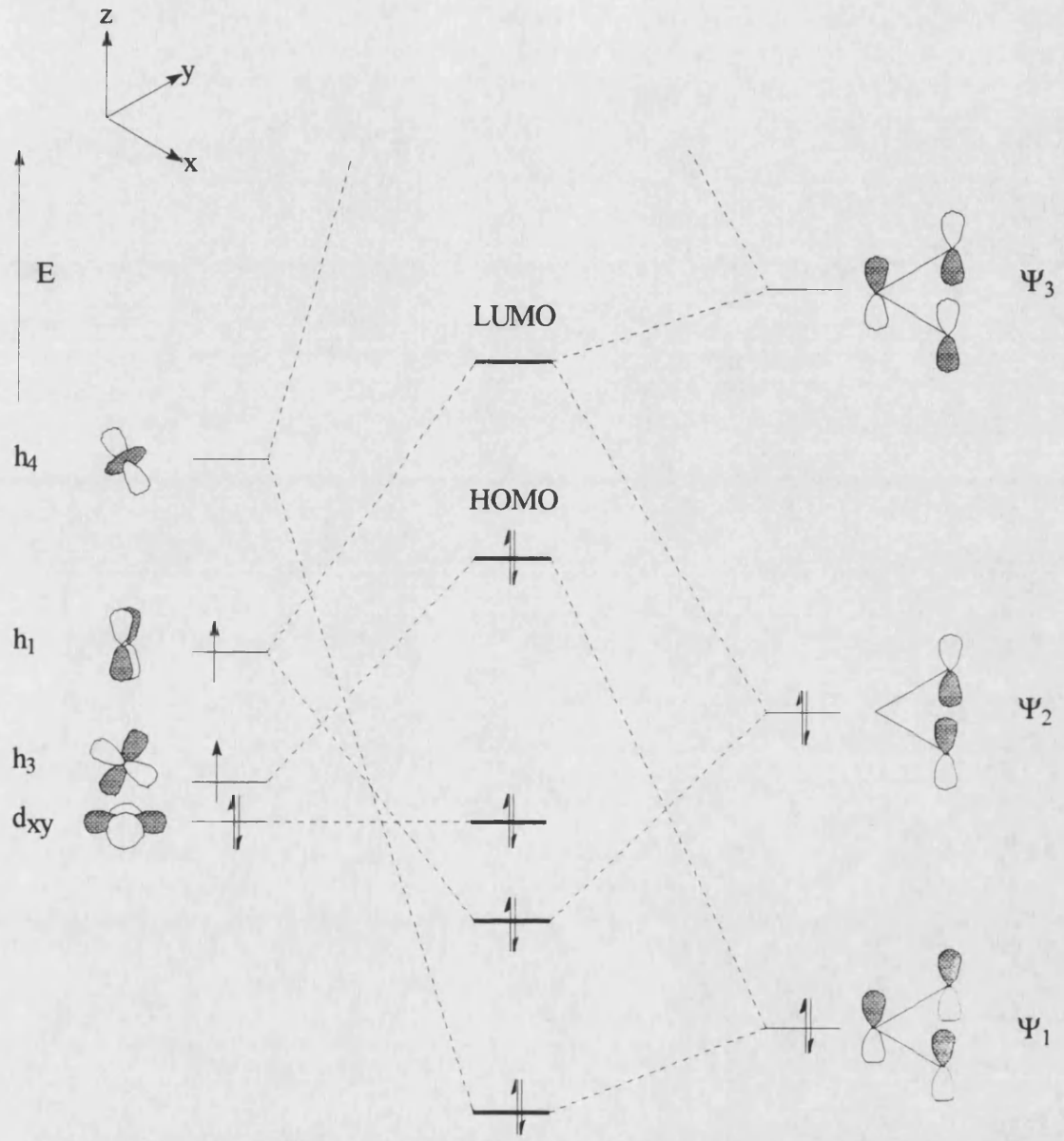
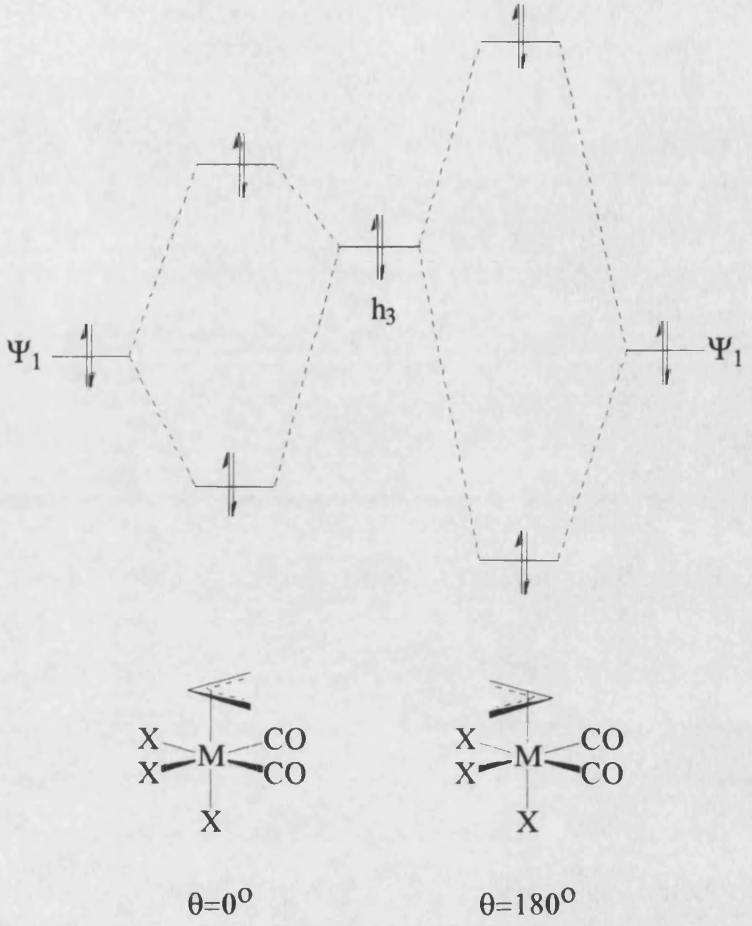


Figure 2.4.7



A further notably consistent feature found in the structure of η^3-allyldicarbonyl complexes is the adoption of "symmetrical" or "unsymmetrical" structures designated **(A)** or **(B)** respectively in **Figure 2.4.8** below. The former contains a plane of symmetry whereas the latter is chiral at the metal centre and exists as enantiomers, only one of which is illustrated.

Figure 2.4.8

Structure (A) **Structure (B)**

Structure **(A)**, in which the η^3-allyl ligand is *trans-* to X and the donor atoms of L_2 lie in an approximate plane with the *cis*-dicarbonyl unit, is by far the more common structure adopted in the solid state. **Table 2.4.1** overleaf lists relevant structural parameters and whether structure type **(A)** or **(B)** is adopted for a range of Group VI complexes of the form $[MXL_2(CO)_2(\eta^3\text{-allyl})]$.

No study has yet provided theoretical reasons as to why structure **(A)** or **(B)** should be preferred but the combination of L_2 and X ligands and/or allyl substitution are significant. Thus, complexes containing π-acceptor ligands (L) adopt structure **(B)** due to the destabilisation which would result from such ligands occupying sites *trans-* to the synergically bonded carbonyl ligands and hence competing for electron density at the metal centre. In some cases, such as the carboxylate complexes $[Mo(O_2CR')(bipy)(CO)_2(\eta^3\text{-}C_3H_5)]$ (R'=CF_3, C_2F_5 or C_3F_7), ^1H NMR studies have shown that in solution at room temperature isomeric forms **(A)** and **(B)** coexist, their relative concentrations being solvent dependent[87]. Isomer **(B)** is dynamic at room temperature whereas **(A)** is not but at higher temperatures interconversion occurs giving rise to a single dynamic species, indicating that a complete *pseudo*rotation of the $(bipy)(O_2CR')$ face has occurred. However the η^3-2-MeC_3H_4 analogues show only structure **(A)** in solution from -90 to +50°C. In this case molecular models have shown

that steric interaction of the inflexible bipy ligand with the larger η^3-2-MeC_3H_4 ligand causes destabilisation of the "unsymmetrical" isomer **(B)** and hence only structure type **(A)** is observed.

Table 2.4.1

Complex	C(1)-C(2) (Å)	C(2)-C(3) (Å)	C(1)-C(2)-C(3) (°)	M-C(1) (Å)	M-C(2) (Å)	M-C(3) (Å)	C(4)-M-C(5) (°)	Structure Type	Ref
[Mo(NCS)(bipy)(CO)$_2$ (η^3-C_3H_5)]	1.440(17)	1.440(17)	115.7(11)	2.291(11)	2.197(9)	2.351(12)	78.3(5)	A	78
[Mo(NCS)(phen)(CO)$_2$ (η^3-C_4H_7)]	1.452(18)	1.404(17)	111.6(11)	2.320(13)	2.274(13)	2.350(12)	82.6(4)	A	79
[Mo(bipy)(py)(CO)$_2$ (η^3-C_3H_5)]BF_4	1.369(13)	1.471(13)	111.4(8)	2.306(8)	2.279(10)	2.290(9)	78.2(3)	A	46
[Mo(O_2CCF_3)$_2$(dme) (CO)$_2$(η^3-C_3H_5)]	1.45(3)	1.45(3)	114(3)	2.34(2)	2.16(3)	2.34(2)	79(1)	A	77
[W(O_2CCF_3)$_2$(dme) (CO)$_2$(η^3-C_3H_5)]	1.36(3)	1.36(3)	123(3)	2.29(2)	2.07(3)	2.29(2)	75(2)	A	77
[MoCl(dppe)(CO)$_2$ (η^3-C_3H_5)]	1.397(17)	1.397(18)	116(1)	2.340(12)	2.221(12)	2.350(17)	77.6(5)	B	67
[Mo(acac)(py)(CO)$_2$ (η^3-C_3H_5)]	1.397(9)	1.371(9)	115.1(6)	2.304(6)	2.202(6)	2.306(7)	79.9(2)	B	68

See **Figure 2.4.1** for numbering scheme.

Table 2.4.1 (cont.)

Complex	C(1)-C(2) (Å)	C(2)-C(3) (Å)	C(1)-C(2)-C(3) (°)	M-C(1) (Å)	M-C(2) (Å)	M-C(3) (Å)	C(4)-M-C(5) (°)	Structure Type	Ref
[Mo(salal)(py)$(CO)_2$ (η^3-C_3H_5)]	1.37(3)	1.42(3)	115.3(17)	2.318(18)	2.241(16)	2.337(17)	79.1(7)	B	82
Et_4N[$WCl_2(PPh_3)(CO)_2$ (η^3-C_3H_5)]	1.47(3)	1.41(2)	114(20	2.33(2)	2.20(2)	2.35(2)	75.6(5)	A	88
[Mo{$Et_2B(pz)_2$}(Hpz) $(CO)_2$(η^3-C_3H_5)]	1.387(6)	1.412(6)	117.2(4)	2.341(4)	2.206(3)	2.347(4)	81.4(2)	A	89
[Mo($PhBpz_3$)$(CO)_2$ (η^3-C_3H_5)]	1.421(10)	1.423(10)	115.6(7)	2.371(8)	2.222(8)	2.343(8)	79.1(3)	A	90
[Mo$(NCMe)_3(CO)_2$ (η^3-C_3H_5)]$^+$	1.47(6)	1.47(6)	117(4)	2.36(5)	2.25(4)	2.35(4)	82.0(18)	A	91
[$Mo_2Cl_3(CO)_4$ (η^3-C_3H_5)$_2$]$^-$	1.38(6)	1.46(6)	118(4)	2.38(4)	2.23(4)	2.30(5)	82.1(16)	A	91
	1.41(7)	1.45(8)	113(5)	2.32(5)	2.18(6)	2.35(5)	78.0(19)	A	91

See **Figure 2.4.1** for numbering scheme.

2.5 Reactivity of Transition Metal η^3-Allyl Complexes

Whilst a comprehensive overview of the reactivity of transition metal η^3-allyl systems is somewhat superfluous to this thesis it is important to note that a vast body of literature has been published[92a-e], reflecting the synthetic utility and versatility of these systems. Much of this has been collected into several review papers[93a-e,94a,b]. In particular, the palladium, molybdenum and nickel systems have been used extensively both as catalysts and in stoichiometric quantities in organic synthesis where the creation of new carbon-carbon bonds has been facilitated by the system's control of S_N2 versus S_N2' nucleophilic attack.

The use of molybdenum as a template to control the regioselectivity of allylic alkylations has been explored extensively by Trost[92c, 92f]. Preformed molybdenum η^3-allyl complexes such as $[MoCl(dppe)(CO)_2(\eta^3\text{-}C_3H_4R)]$ (R=H, Me) and $[MoCl(bipy)(CO)_2(\eta^3\text{-}C_3H_4Me)]$ were employed in the allylic alkylation of 2-carbomethoxycyclopentanone to establish the feasibility of the alkylation step. The complexes $[Mo(bipy)(CO)_4]$, $[Mo(dppe)(CO)_4]$ and $[Mo(TMEDA)(CO)_4]$ were then employed as catalysts in the reaction between crotyl acetate and the anion of 2-carbomethoxycyclopentanone but were found to be rather unreactive. In contrast the catalysts $[Mo(CO)_6]$ and in particular $[Mo(CNR)_4(CO)_2]]$ (R=*t*-C_4H_9, *n*-C_4H_9, Ph, 2,6-$(CH_3)_2C_6H_3$) have proved to be extremely effective catalysts in a wide range of allylic alkylations both in terms of reactivity and their ability to exert regioselective control over the attack of the alkylating agent.

The formation of η^4-trimethylenemethane complexes from transition metal η^3-allyl complexes is covered in depth in **Section 3**.

2.6 DISCUSSION

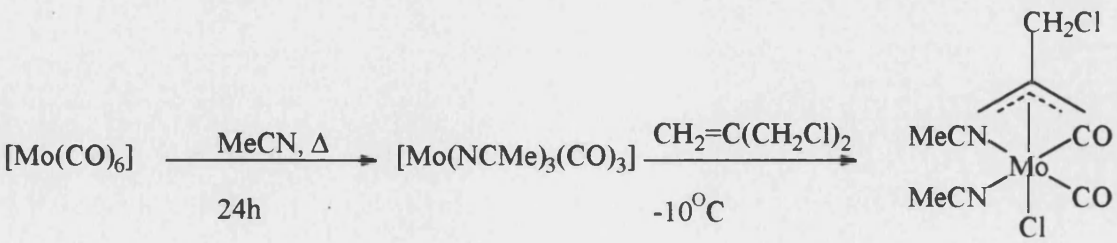
The preparations discussed in this section concern the synthesis of various 2-substituted-allyl Mo(II) derivatives which have the potential to undergo conversion to η^4-trimethylenemethane complexes and attempts to do this, generally by abstraction of HCl or MeOH from the allyl complexes, are described in the **Section 3.4**.

Preparation of 2-Substituted-Allyl Mo(II) Complexes

2.6.1 Preparation of $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (1)

The synthesis of complex (**1**) was reported in 1986 by Baker[95], *via* a two-stage one-pot preparation involving the conversion of molybdenum hexacarbonyl into the tris-acetonitrile derivative $[Mo(CO)_3(NCMe)_3]$, which subsequently undergoes an oxidative addition with 3-chloro-2-chloromethylpropene to give (**1**) in high yield (85%) (**Scheme 2.6.1**). A one-stage direct synthesis in which molybdenum hexacarbonyl and 3-chloro-2-chloromethylpropene were heated together in acetonitrile was found to afford only decomposition products.

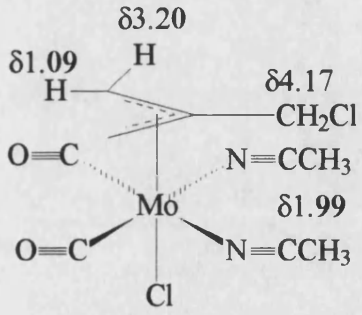
Scheme 2.6.1



Complex (1)

A slightly modified procedure was adopted in this study. Refluxing molybdenum hexacarbonyl for only 2.5 hours in acetonitrile, followed by the addition of 3-chloro-2-chloromethylpropene at 0°C, was found to give comparable yields of the required complex. The bright yellow compound thus formed does not require further purification. Satisfactory elemental analyses were obtained and complex (**1**) had a ν(C≡N) band in its infra-red spectrum centred at 2315cm^{-1}, and two ν(C≡O) bands at 1962 and 1869 cm^{-1} in close agreement to the published results and consistent with a *pseudo*-octahedral, *cis*-dicarbonyl geometry. The ^{1}H NMR spectrum of complex (**1**), obtained in D_2O, contained a two proton singlet at δ4.17, corresponding to the 2-substitution on the allyl group. The pairs of *syn* and *anti*-protons resonate as singlets at δ3.20 and 1.09 respectively, whilst the two methyl cyanide ligands gave a six proton singlet at δ1.99 (**Figure 2.6.1**). Complex (**1**) was found to decompose slowly at room temperature and was thus kept at 0°C.

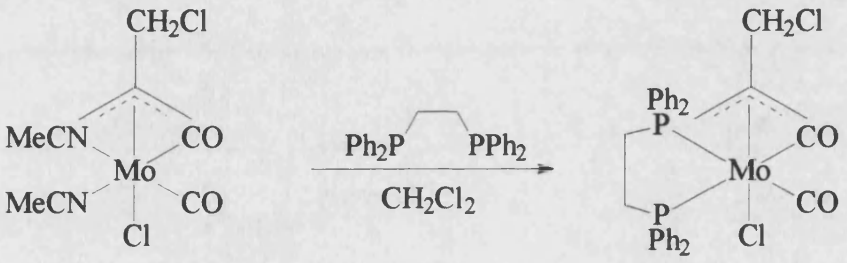
Figure 2.6.1



2.6.2 Attempted preparation of [MoCl(dppe)(CO)$_2${η^3-$CH_2C(CH_2Cl)CH_2$}] (2)

The paper cited above for the preparation of complex (**1**) contained a brief, preliminary account of the preparation of complex (**2**) *via* the reaction of complex (**1**) with an equimolar quantity of 1,2-bis(diphenylphosphino)ethane (dppe) (**Scheme 2.6.2**). No further details of the isolation and characterisation of this complex were included.

Scheme 2.6.2



Complex (1) **Complex (2)**

Accordingly, in an attempt to generate a more stable η^3-$C_3H_4CH_2Cl$ containing derivative, complex (**1**) was reacted with dppe at room temperature in CH_2Cl_2. The reaction mixture immediately turned a deeper yellow upon the addition, and infra-red monitoring of the stirred reaction mixture after 0.25h showed the expected shifting of the carbonyl bands to lower wavenumber (1931, 1833cm^{-1}). Removal of the reaction solvent *in vacuo* left a yellow residue which had a similar infra-red pattern. However attempts to recrystallise this solid from a variety of organic solvents generally led to the formation of intractable tars. Unsatisfactory analytical results were also obtained for the solid formed upon direct treatment of the reduced volume reaction liquors with 40-60° petroleum ether. Column chromatography was also unsuccessful as a purification technique and NMR data

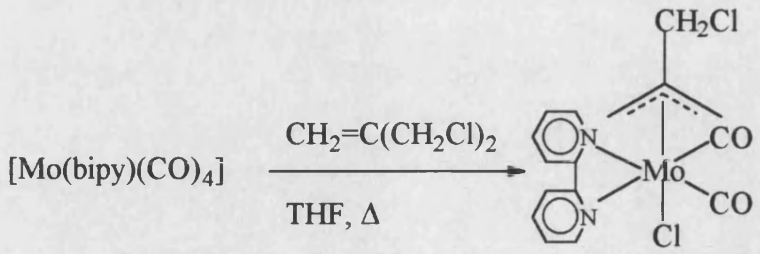
on the crude material was very complex. Further attempts at preparing complex (**2**) were abandoned.

Possible reasons for the failure of this displacement reaction to occur cleanly, as occurs in reactions involving $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2C(CH_3)CH_2\}]$, may include steric hindrance, with the bulky phosphine prevented from facile complexation with the metal by the $-CH_2Cl$ moiety. Interaction of the basic phosphine with the $-CH_2Cl$ containing allyl substituent, leading to the elimination of an allylphosphonium halide and the formation of an unstable Mo(0) species which decomposes in solution is another possibility. Consequently a different bidentate ligand was used.

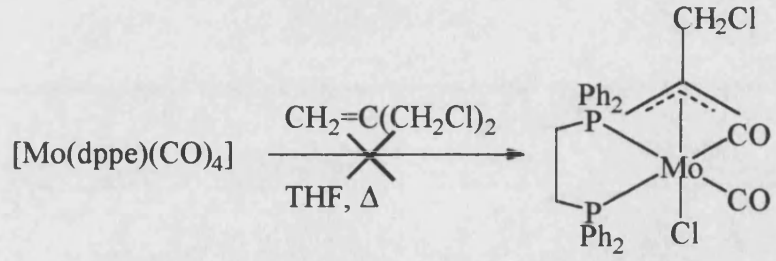
2.6.3 Preparation of $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (3)

The displacement of the two methyl cyanide ligands of complex (**1**) by the bidentate 2,2'-bipyridyl ligand was attempted using a similar procedure to that described above. The reaction mixture turned a deep red colour in the course of the reaction, and an infra-red spectrum taken after 0.25h indicated that reaction had taken place. However, as with the dppe product, similar problems with the purification of the crude material exacerbated by limited solubility were encountered. However direct reaction of $[Mo(bipy)(CO)_4]$ with 3-chloro-2-chloromethylpropene in refluxing THF proceeded smoothly, to afford complex (**3**) in 85% yield (**Scheme 2.6.3**). In this case the 2,2'-bipyridyl ligand is already bound to the metal and does not interfere with the chloroallyl ligand. An attempt to prepare complex (**2**) from $[Mo(dppe)(CO)_4]$ in a similar manner did not succeed. However, this is not a viable route for other phosphine substituted allyl derivatives of the form $[MoXL_2(CO)_2(\eta^3\text{-allyl})]$.

Scheme 2.6.3



Complex (3)



Complex (2)

Complex (**3**) gave satisfactory elemental analyses without further purification and exhibited ν(C≡O) modes in the infra-red region at 1939 and 1863cm^{-1}. The ^{1}H NMR spectrum of complex (**3**) could not be determined as it is insoluble except in highly polar organic solvents such as DMSO, in which it appears to decompose. Attempts to improve the solubility of the complex by reaction with NaO_2CCF_3, thus replacing the chloride ligand with trifluoroacetate, were unsuccessful. A complex mixture of unidentifiable molybdenum species were formed suggesting that the trifluoroacetate anion attacks the -CH_2Cl moiety as well as the metal centre.

2.6.4 Attempted preparation of $[Mo\{HN(CH_2CH_2NH_2)_2\}(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}][PF_6]$ (4)

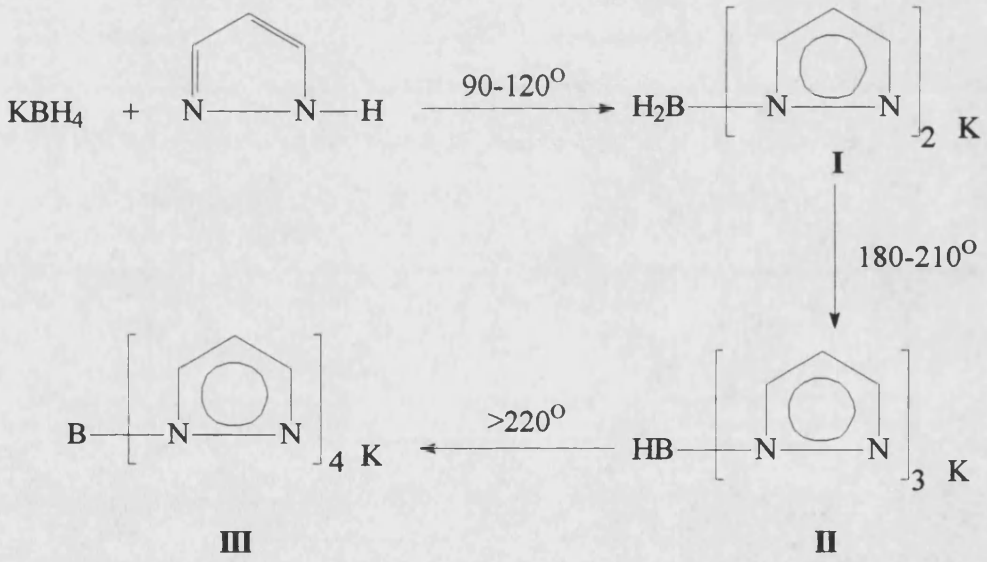
This type of complex, but containing η^3-C_3H_5 or η^3-2-MeC_3H_5 ligands, was first prepared in these laboratories by Hodson[96] *via* the reaction of $[MCl(NCMe)_2(CO)_2(\eta^3\text{-}2\text{-}C_3H_4R)]$ with excess diethylenetriamine (dien) or bis-(2-pyridylmethyl)amine (bpma) in aqueous solution. On addition of ammonium hexafluorophosphate the complexes $[M(CO)_2(\eta^3\text{-}2\text{-}C_3H_4R)L_3][PF_6]$ (M=Mo, W; R=H, Me; L_3=dien or bpma), in which the dien or bpma acts as a tridentate ligand, could be isolated.

In an attempt to apply this reaction to η^3-$ClCH_2C_3H_4$ complexes, and so generate a stable cationic derivative, complex (**1**) was stirred with diethylenetriamine in water for 1h, after which an aqueous solution of ammonium hexafluorophosphate was added. No precipitate was forthcoming at this stage and slow evaporation of the reaction solvent over concentrated sulphuric acid gave only unidentifiable mixtures of Mo species. Repeating this procedure with acetonitrile rather than water as solvent yielded a very small amount of a yellow solid which had spectral and analytical data consistent with that expected for complex (**4**). However, given the very small yield (<5%) and the presence of other products in this reaction, this route was not pursued. It appears quite likely that the dien, rather than acting only as a tridentate ligand, is also attacking the -CH_2Cl moiety of complex (**1**). Therefore attempts were made to prepare an analogue containing a N-based tridentate ligand without reactive N-H linkages.

2.6.5 Attempted preparation of $[Mo(CO)_2\{HB(Pz)_3\}\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (5) ($HB(Pz)_3$=hydrotris(1-pyrazolyl)borato)

The poly(1-pyrazolyl)borates $K[R_nB(Pz)_{4-n}]$ first developed by Trofimenko[96-103] have proved to be a versatile class of uninegative ligands which, through coordination of a nitrogen from the pyrazolyl group, can act as either bi- or tri-dentates on complexation with organometallic compounds. The synthesis of these compounds involves reaction between potassium borohydride and a large excess of molten pyrazole, leading to dihydrobis-, hydrotris- or tetrakis(1-pyrazolyl)borates (**I-III** respectively below) depending on the temperature chosen (**Scheme 2.6.4**).

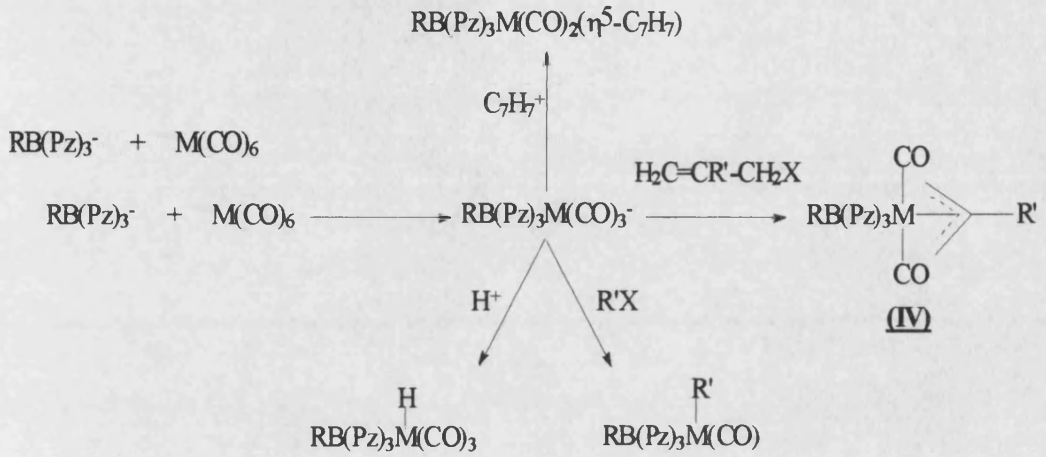
Scheme 2.6.4



The reactions of hydrotris(1-pyrazolyl)borate and tetrakis(1-pyrazolyl)borate with group (VI) metal carbonyls led to a wide range of novel tridentate-substituted

organometallics, including many molybdenum or tungsten allyl complexes (**IV**) as shown in **Scheme 2.6.5**[101].

Scheme 2.6.5



(IV):- M=Cr; R=Pz; R'=H
M=Mo; R=H, Pz; R'=H, CH_3, C_6H_5, Br
M=W; R=H, Pz; R'=H, CH_3

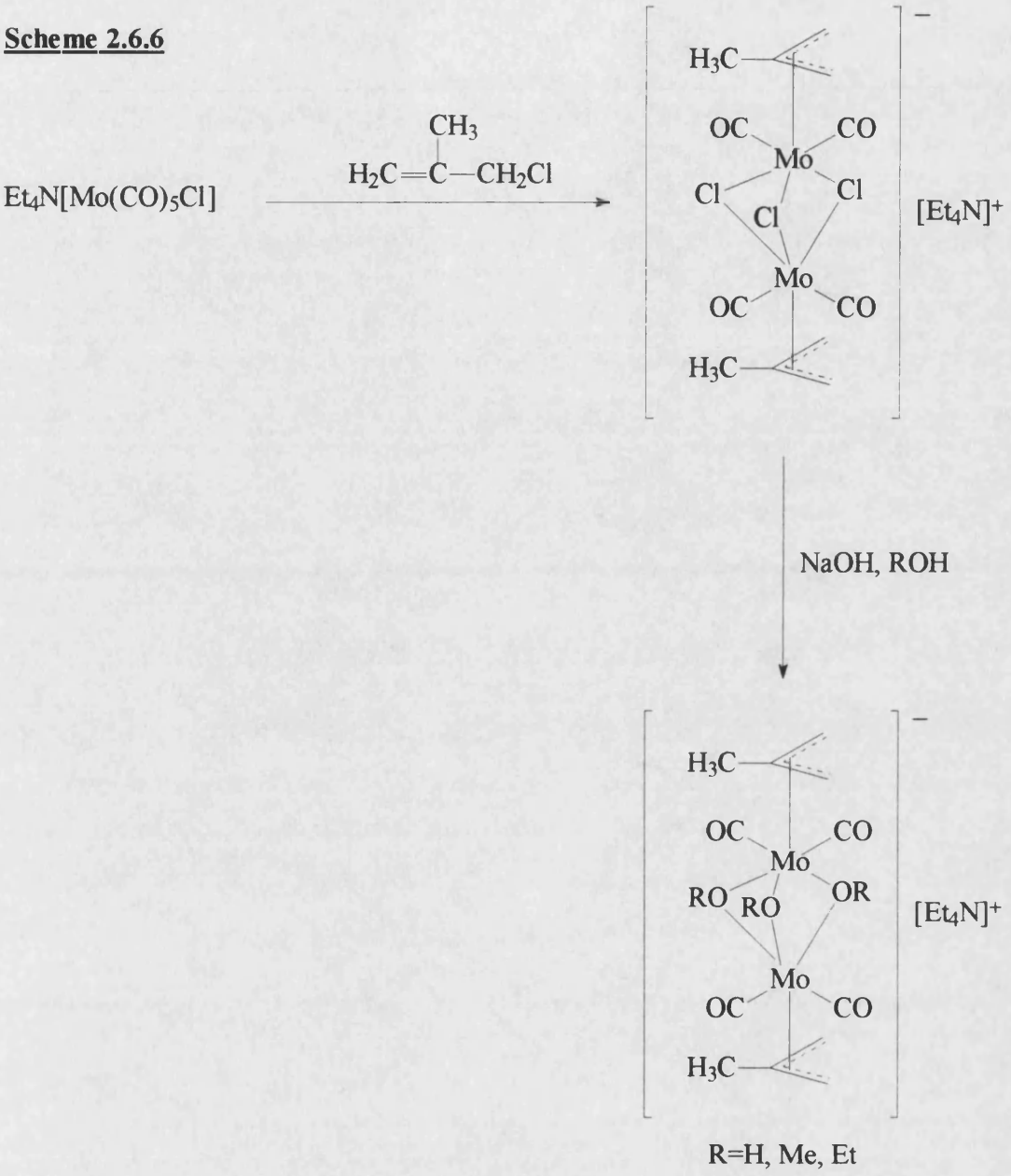
Thus, in the hope of preparing a more stable derivative of complex (**1**) $K[Mo(CO)_3\{HB(Pz)_3\}]$ was first prepared and treated with 3-chloro-2-chloromethylpropene at 40°C. The reaction mixture was heated to 80°C before any effervescence was observed. An infra-red spectrum of the reaction mixture taken at this point indicated the co-existence of several molybdenum species. However, after working-up the reaction according to literature procedures, the only solid obtained proved to be a non-carbonyl containing species. An attempt made to react $K[HB(Pz)_3]$ directly with complex (**1**) in acetonitrile at 45°C followed by pouring the reaction mixture into water containing a small amount of HCl to neutralise any remaining $[HB(Pz)_3]^-$ was also unsuccessful. The common thread running through all these reactions was the apparent

reactivity of the η^3-$ClCH_2C_3H_4$ moiety compared with the comparatively inert η^3-$CH_3C_3H_4$ group.

2.6.6 Reaction of [MoCl(NCMe)$_2$(CO)$_2${CH$_2$C(CH$_2$Cl)CH$_2$}] (1) with basic ROH (R=H, Me, Et) and R'$_4$XCl (R'=Ph, X=As; R'=Et, X=N)

The dimeric complexes $Et_4N[Mo_2(CO)_4(\eta^3\text{-}2\text{-}C_3H_4Me)_2\mu\text{-}(X)_3]$ (X=Cl, OH, OMe, OEt) were prepared initially by Murdoch[104] in 1965. The hydroxy-, methoxy- and ethoxy-bridged complexes were synthesised from the tri-μ-chloro complex by reaction with sodium bases in water, methanol or ethanol (**Scheme 2.6.6**).

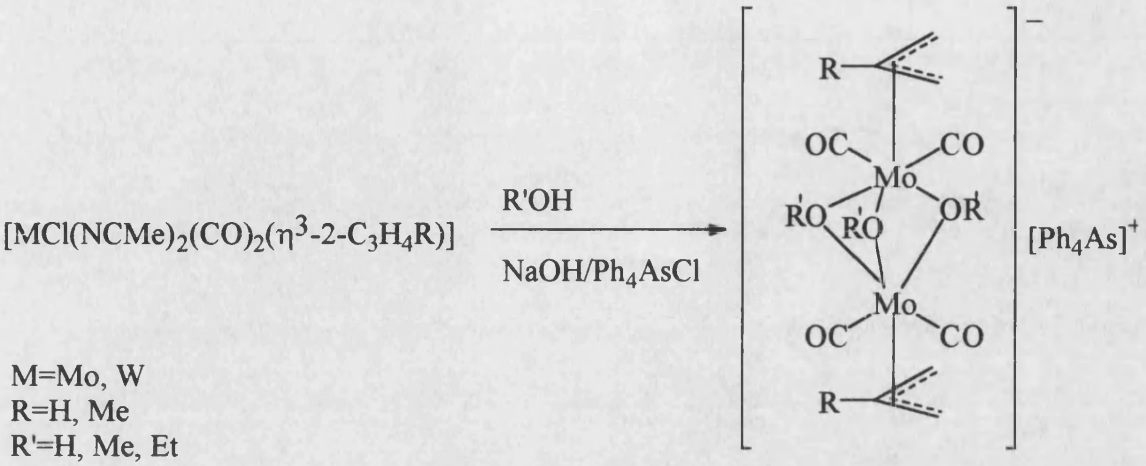
Scheme 2.6.6



R=H, Me, Et

In an investigation into the solution properties of $[MCl(NCMe)_2(CO)_2(\eta^3\text{-}2\text{-}C_3H_4R)]$ (M=Mo or W; R=H, Me), Hodson[96] prepared the tetraphenylarsonium salts of the above alkoxy-bridged complexes by reacting the monomeric alkyls with Ph_4AsCl in basic hydroxylic solvents (**Scheme 2.6.7**).

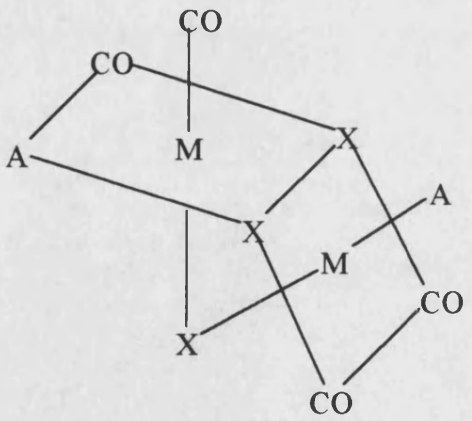
Scheme 2.6.7



M=Mo, W
R=H, Me
R'=H, Me, Et

The products were found to contain four strong carbonyl bands in their infra-red spectra occurring, as expected, at lower wavenumbers than the halo-bridged analogues and consistent with a confacial bi-octahedral structure, as in the original μ-Cl complexes (**Figure 2.6.2**).

Figure 2.6.2



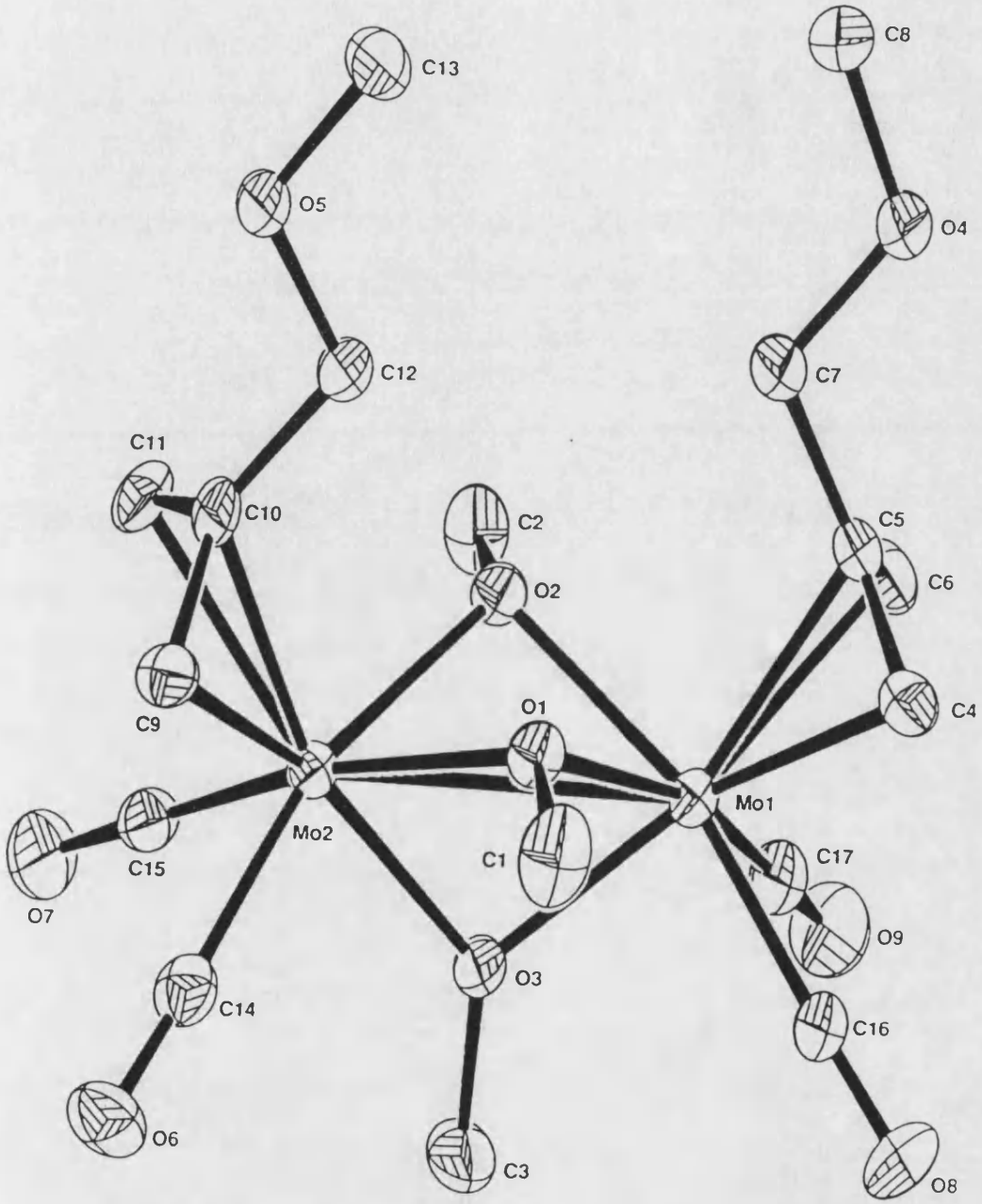
M=Metal
A=Allyl
X=OR'

The ^1H NMR spectra of these complexes showed that two of the three alkoxy bridges are in equivalent magnetic environments, with the third unique, and that the two allyl groups are either in identical environments or are dynamic about the metal-allyl bond.

This reaction was extended to complex (**1**), which was dissolved in methanol and treated with Ph_4AsCl in aqueous 1M NaOH. An immediate yellow precipitate occurred which on recrystallisation gave complex (**6**). The infra-red spectrum of complex (**6**) contained two carbonyl bands centred at 1904 and 1802cm^{-1}, both of which exhibited a slight splitting. An additional C-O stretching vibration occurred at 1065cm^{-1}. The ^1H NMR spectrum, obtained in $CDCl_3$,contained a twenty proton multiplet centred at δ7.94, corresponding to the aromatic protons of the cation, with the unique and two equivalent methoxy-bridges appearing as 3- and 6-proton singlets at δ4.96 and 3.70 respectively. The allyl *syn* and *anti* protons resonated as 4-proton singlets at δ3.56 and δ0.57, together with an extra 6-proton singlet at δ3.48. Correlating this observation with the elemental analyses obtained for complex (**6**), it is apparent that the chlorine of the $-CH_2Cl$ moiety has been replaced completely by a methoxy group, the product thus being $Ph_4As[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$. By synthesising the analogous tetraethylamine salt of complex (**6**), crystals suitable for an X-ray diffraction study were obtained and the methoxy-substitution confirmed (**Figure 2.6.3**). The crystal structure of $Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$ (**9**) is discussed below.

Attempts to prepare the ethoxy-bridged analogue (**7**) of complex (**6**) by a similar procedure using ethanol as the reactant solvent, led to the formation of mixtures which could not be separated by recrystallisation. It appears that the bulkier ethoxide ion does not completely replace chlorine in the allyl substituent. By using water as the reaction solvent it was hoped that the tris-μ-hydroxy analogue (**8**) of complex (**6**) could be prepared. A yellow solid was indeed obtained from this reaction but attempts at recrystallisation led to partial decomposition.

Figure 2.6.3


C13
C8
O5
O4
C12
C7
C11
C10
C2
C5
O2
C6
C9
O1
C4
Mo2
Mo1
C15
C1
C17
O7
O9
O3
C14
C16
O6
C3
O8

THE CRYSTAL STRUCTURE OF $Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$ (9)

Figure 2.6.3 on the previous page shows an ORTEP view of complex (**9**) along with the atomic numbering scheme employed whilst **Table 2.6.1** below summarises the major bond lengths and bond angles in the complex.

Table 2.6.1

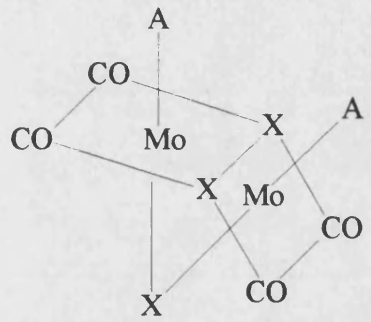
Bond	**Length (Å)**	**Bond**	**Length (Å)**	**Bond**	**Angle (°)**
Mo1-Mo2	3.155(1)			Mo2-O1-Mo1	92.9(1)
Mo1-O1	2.160(4)	Mo2-O1	2.192(4)	Mo2-O2-Mo1	92.2(1)
Mo1-O2	2.189(4)	Mo2-O2	2.191(4)	Mo2-O3-Mo1	97.7(2)
Mo1-O3	2.092(4)	Mo2-O3	2.099(4)	C4-C5-C6	115.3(6)
Mo1-C4	2.309(8)	Mo2-C9	2.315(6)	C9-C10-C11	115.7(6)
Mo1-C5	2.210(7)	Mo2-C10	2.220(6)		
Mo1-C6	2.339(8)	Mo2-C11	2.333(7)		
C4-C5	1.417(10)	C9-C10	1.426(9)		
C5-C6	1.414(10)	C10-C11	1.404(10)		
C5-C7	1.495(9)	C10-C12	1.488(9)		

Thus, it can be seen that the C-C and M-C bond lengths and angles found in complex (**9**) are typical for those expected of a molybdenum η^3-allyl complex. In particular the data were similar to those obtained for the crystal structure of the related chloride-bridged molybdenum complex $[Mo_2(\mu\text{-}Cl)_3(CO)_4(\eta^3\text{-}C_3H_5)_2]^-$ (see **Table 2.4.1**). However $Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3)]$ has a much

more regular and symmetrical structure than the chloride-bridged analogue with both allyl moieties having very similar C-C and M-C bond lengths and internal angles. In addition whilst one allyl group is axial and the other equatorial in the chloride-bridged dimer, both allyl groups in complex (**9**) are axial as depicted in **Figure 2.6.4** below.

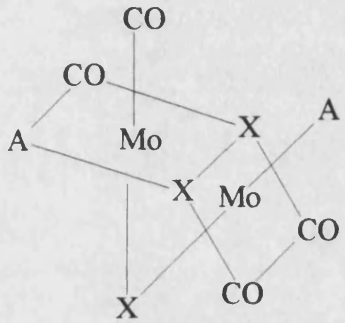
Figure 2.6.4:-*Comparison of the allyl orientation in complex (9) and $[Mo_2(\mu\text{-}Cl)_3(CO)_4(\eta^3\text{-}C_3H_5)_2]^-$*

Complex (9) **$[Mo_2(\mu\text{-}Cl)_3(CO)_4(\eta^3\text{-}C_3H_5)_2]^-$**



A=η^3-$CH_2C(CH_2OMe)CH_2$

X=OMe



A=η^3-C_3H_5

X=Cl

Thus it would appear that these bridged dimers are isomers of each other in a similar manner to the isomers of complexes of the type $[ML_2X(CO)_2(\eta^3\text{-allyl})]$ which exist in "symmetrical" and "unsymmetrical" forms as discussed earlier in **Section 2.4**. Indeed complex (**9**) can be considered to be a combination of two units of the "symmetrical" monomer and $[Mo_2(\mu\text{-}Cl)_3(CO)_4(\eta^3\text{-}C_3H_5)_2]^-$ as a combination of a "symmetrical" and an "unsymmetrical" unit. The ^1H NMR data for complex (**9**) show only one set of allyl signals as expected as both allyl units are in similar environments, whilst the methoxy bridges appear as a 6 proton singlet (for the two methoxy groups *trans*- to carbonyl

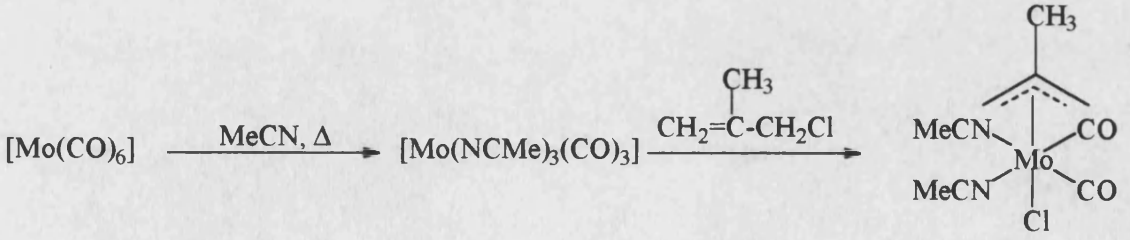
moieties) and a 3 proton singlet (for the unique methoxy group which is *trans*- to the allyl moieties).

As can be seen from the data above in **Table 2.6.1** the Mo-Mo distance in complex (**9**) is about 3.16Å whilst calculations show the Mo-Mo distance in $[Mo_2(\mu\text{-}Cl_3)(CO)_4(\eta^3\text{-}C_3H_5)_2]^-$ to be about 3.55Å. The longest known Mo-Mo bond distance in an *unbridged* complex is 3.24Å in the case[106] of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ whilst non-bonding Mo-Mo distances in *bridged* complexes[107-109] are generally of the order of ~3.3-3.6Å. Complexes in which there is a known Mo-Mo bond have a M-M bond length of around 2.6-2.75Å in the case of several Mo(III) complexes[110-113]. Thus, while there may be some sort of Mo-Mo interaction in complex (**9**), it cannot be considered as a significant bond.

2.6.7 Preparation of $[Mo(NCMe)_2Cl(CO)_2\{\eta^3\text{-}2\text{-}C_3H_4Me\}]$ (10)

Complex (**10**) was prepared in 47% yield according to a literature method[2], *via* the reaction of $[Mo(NCMe)_3(CO)_3]$ with 3-chloro-2-methylpropene in acetonitrile (**Scheme 2.6.8**).

Scheme 2.6.8

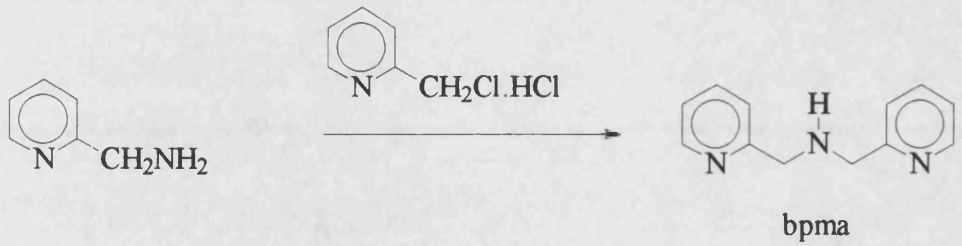


Complex (10)

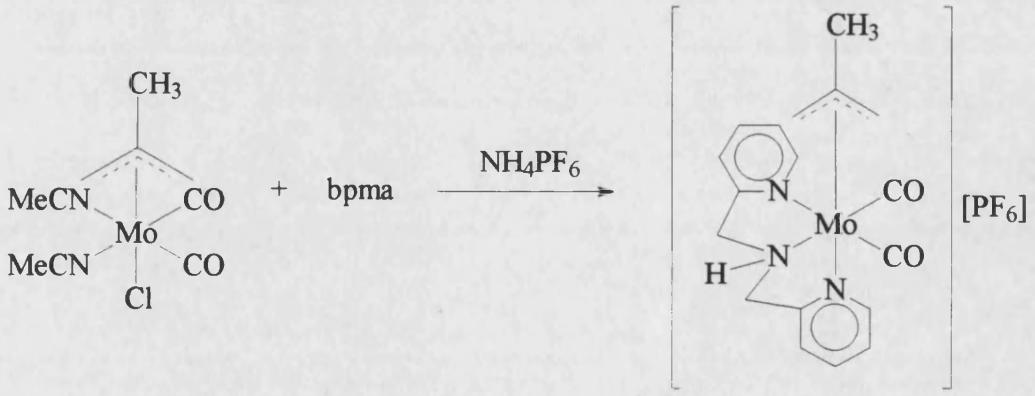
2.6.8 Preparation of [Mo(bpma)(CO)$_2${η^3-2-C_3H_4Me}][PF_6] (11)

Bis(2-pyridylmethyl)amine (bpma) was prepared from 2-chloromethylpyridine hydrochloride and 2-aminopyridine and reacted with complex (**10**) to give complex (**11**) again following a published method[105] (**Scheme 2.6.9**).

Scheme 2.6.9



bpma



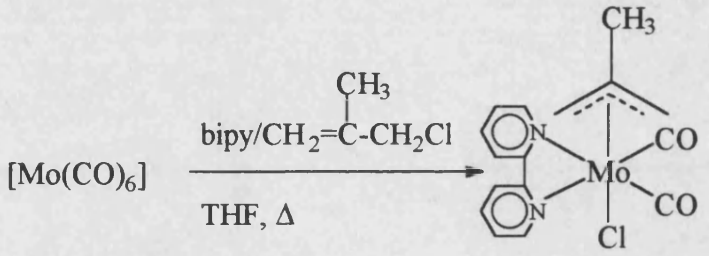
Complex (10) **Complex (11)**

It was envisaged that complex (**11**) might lose a proton from the allyl-methyl substituent, thus giving a neutral η^4-trimethylenemethane complex as discussed in **Section 3.4**.

2.6.9 Preparation of [MoCl(bipy)(CO)$_2${η^3-2-C_3H_4Me}] (12)

Complex (**12**) was prepared according to a literature procedure[3,6] in 70 % yield (**Scheme 2.6.10**).

Scheme 2.6.10



Complex (12)

2.6.10 Conclusions

The reactions discussed above show that the -CH_2Cl substituent in the η^3-allyl moiety is remarkably reactive towards bases. Under conditions in which the MeCN ligands of [MoCl(NCMe)$_2$(CO)$_2$(η^3-2-C_3H_4Me)] are replaced with bidentates and tridentate ligands complex (**1**) decomposes. Only in the case of reaction in basic methanol, in which the C-Cl bond in the ligand is completely solvolysed was a pure product formed from complex (**1**).

Attempts to convert complexes (**1**), (**3**), (**6**), (**11**) and (**12**) into η^4-trimethylenemethane derivatives are discussed in **Section 3.4**.

2.7 EXPERIMENTAL

Starting materials:-

The complexes $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}2\text{-}C_3H_4Me\}]$ **(10)**, $[Mo(bpma)(CO)_2\{\eta^3\text{-}2\text{-}C_3H_4Me\}][PF_6]$ **(11)**, $[MoCl(bipy)(CO)_2\{\eta^3\text{-}2\text{-}C_3H_4Me\}]$ **(12)** and bis(2-pyridylmethyl)amine (bpma) were prepared according to published methods[2,3,6,105].

2.7.1 Preparation of $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (1)

A solution of $[Mo(NCMe)_3(CO)_3]$ was prepared by heating under reflux molybdenum hexacarbonyl (2.64g, 10.00mmol) in acetonitrile ($30cm^3$) for 2.5h. To the cooled solution (0°C) was added dropwise with stirring, 3-chloro-2-chloromethylpropene ($2.20cm^3$, 19.80mmol), which caused an immediate effervescence. After stirring at room temperature for 0.5h, the reaction mixture was refrigerated overnight and filtered, yielding a yellow solid which was washed with 10:1 ether/acetonitrile ($50cm^3$) and dried to give **(1)** in somewhat variable yields (50-80%).

Infra-red: $\nu(C\equiv N)$ $2315cm^{-1}$; $\nu(C\equiv O)$ 1962, $1869cm^{-1}$

NMR (^1H, D_2O, 270MHz): δ4.17 (2H, s, $C\underline{H}_2Cl$); 3.20 (2H, s, *syn* protons); 1.99 (6H, s, $C\underline{H}_3CN$); 1.09 (2H, s, *anti* protons)

Microanalysis: Found; C, 33.4; H, 3.37; N, 7.68%. Calculated for $C_{10}H_{12}Cl_2MoN_2O_2$; C, 33.45; H, 3.37; N, 7.80%

2.7.2.1 Attempted preparation of [MoCl(dppe)(CO)$_2${η^3-$CH_2C(CH_2Cl)CH_2$}] (2) from complex (1)

To a solution of 1,2-bis(diphenylphosphino)ethane (1.00g, 2.51mmol) in dichloromethane (10cm^3) was added complex (**1**) (0.75g, 2.09mmol). After stirring the reaction mixture at room temperature for 1h, the solvent was removed *in vacuo* to leave a pale yellow solid. Attempts to recrystallise the crude solid proved unsuccessful and microanalytical and ^{1}H NMR data on the crude product were inconsistent with the pure product. Similar results were obtained on repeating the above procedure, whilst an attempt to precipitate the material directly from the reaction solution by the addition of 40-60° petroleum ether led only to the recovery of the aforementioned crude solid.

Infra-red: ν(C≡O) 1937, 1842cm^{-1}

NMR (^{1}H, DMSO-d^6, 270MHz): δ8.15-7.35 (20H, m); 5.77 (1H, s); 5.37 (0.2H, t); 4.97-4.91 (0.5H, d, J=22.3Hz); 3.96 (~1H, m); 3.69-3.65 (~0.7H, d, J=11.5Hz); 2.24 (~2H, m); 2.08 (0.2H, s); 0.50 (~0.3H, s); 0.36 (~0.3H, m)

Microanalysis: Found; C, 52.9; H, 4.48; N, 0%; Calculated for $C_{32}H_{30}Cl_2MoO_2P_2$; C, 56.91; H, 4.48; N, 0%

2.7.2.2 Attempted preparation of [MoCl(dppe)(CO)$_2${η^3-$CH_2C(CH_2Cl)CH_2$}] (2) from [Mo(dppe)(CO)$_4$]

A mixture of [Mo(dppe)(CO)$_4$] (0.50g, 0.82mmol) and 3-chloro-2-chloromethylpropene (0.50cm^3, 4.3mmol) in THF (20cm^3) was heated under reflux for 4h. Infra-red monitoring of the reaction mixture showed only starting materials with no evidence of any product formation and the reaction was discontinued.

2.7.3.1 Attempted preparation of [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CH_2Cl)CH_2$}] (3) from complex (1)

To a solution of 2,2'-bipyridyl (0.24g, 1.53mmol) in dichloromethane (25cm^3) was added complex (**1**) (0.50g, 1.39mmol). The reaction solution turned a dark-red immediately, and after stirring at room temperature for 1h, the solvent was removed *in vacuo* leaving a dark red solid. Attempts to recrystallise this crude material from a variety of organic solvents and solvent mixtures were unsuccessful. Analytical data were variable and inconsistent with a completely pure product (the best analysis is given below) and the following route (**2.7.3.2**) leading directly to an apparently pure product was thus followed.

Infra-red: ν(C≡O) 1940, 1850cm^{-1}

NMR Complex is soluble only in highly polar solvents such as DMSO in which it appears to decompose

Microanalysis: Found; C, 43.1; H, 3.30; N, 6.41%. Calculated for $C_{16}H_{14}Cl_2MoN_2O_2$; C, 44.37, H, 3.26; H, 6.47%

2.7.3.2 Preparation of [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CH_2Cl)CH_2$}] (3) from [Mo(bipy)(CO)$_4$]

A mixture of [Mo(bipy)(CO)$_4$] (1.00g, 2.75mmol) and 3-chloro-2-chloromethylpropene (0.95cm, 8.21mmol) in THF (30cm^3) was heated under reflux for 2.5h before being cooled, refrigerated overnight and filtered. The resultant red solid was washed with THF and diethyl ether and dried to give (**3**).

Yield=1.01g (85%)

Infra-red: ν(C≡O) 1939, 1863cm^{-1}

NMR Complex (**3**) is soluble only in highly polar solvents apart from DMSO in which it appears to decompose

Microanalysis: Found; C, 44.3; H, 3.21; N, 6.46%. Calculated for $C_{16}H_{14}Cl_2MoN_2O_2$; C, 44.37; H, 3.26; N, 6.47%

2.7.4.1 Attempted preparation of $[Mo\{HN(CH_2CH_2NH_2)_2\}(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}][PF_6]$ (4)

To a stirred solution of $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (**1**) (0.50g, 1.39mmol) in water ($15cm^3$) was added diethylenetriamine ($0.16cm^3$, 1.48mmol). After heating under reflux for 1h, a solution of ammonium hexafluorophosphate (0.23g, 1.43mmol) in water ($1cm^3$) was added to the cooled reaction mixture. No precipitate was observed at this stage and prolonged standing of the reaction mixture in a desiccator over concentrated sulphuric acid led to the decomposition of the reaction products.

2.7.4.2 Preparation of $[Mo\{HN(CH_2CH_2NH_2)_2\}(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}][PF_6]$ (4)

To a stirred solution of $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (**1**) (0.50g, 1.39mmol) in acetonitrile ($15cm^3$) was added diethylenetriamine ($0.16cm^3$, 1.48mmol). After stirring at room temperature for 1h, the resulting yellow precipitate was filtered off and redissolved in water ($12cm^3$). Ammonium hexafluorophosphate (0.23g, 1.42mmol) was then added and the yellow precipitate thus formed was filtered off. Further evaporation of the filtrate by prolonged standing over concentrated sulphuric acid did not lead to the recovery of further material. Repetition of the above procedure gave similarly small yields and, given the likelihood of an extensive number of by-products being formed, this reaction was not pursued any further.

Yield=38mg(5%)

Infra-red: ν(C≡O) 1943, 1840cm^{-1}

NMR (^{1}H, CD_3COCD_3, 270MHz): δ7.45 (~0.3H, br m); 4.2-2.97 (~10H, br m); 1.15 (~1H br m) (all peaks are very broad and poorly resolved, no fine structure can be discerned and the complex appears to be dynamic)

Microanalysis: Found; C, 24.6; H, 4.29; N, 8.98%.

Calculated for $C_{10}H_{19}ClF_6MoN_3O_2P$; C, 24.52; H, 3.91; N, 8.58%

2.7.5.1 Attempted preparation of [Mo(CO)$_2${HB(Pz)$_3${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (5) (HB(Pz)$_3$=hydrotris(1-pyrazolyl)borato)

A solution of K[Mo(CO)$_3${HB(Pz)$_3$}] was prepared by heating at 100°C for 3h in dimethylformamide (25cm^3) a stirred mixture of [Mo(CO)$_6$] (1.32g, 5.00mmol) and K[HB(Pz)$_3$] (1.72g, 5.10mmol). After cooling to ~40°C, 3-chloro-2-chloromethylpropene (0.90cm^3, 7.78mmol) was added dropwise with stirring. No effervescence was observed until the reaction temperature had been increased to 80°C. An infra-red spectrum taken at this point showed the existence of several molybdenum species in solution. The reaction mixture was then poured into water (20cm^3) and the reaction products extracted with dichloromethane. However, only non-carbonyl containing materials were obtained after evaporation of the dichloromethane and the reaction was abandoned at this stage.

2.7.5.2 Attempted preparation of [Mo(CO)$_2${HB(Pz)$_3${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (5) (HB(Pz)$_3$=hydrotris(1-pyrazolyl)borato)

A stirred mixture of [MoCl(NCMe)$_2$(CO)$_2${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (1) (1.00g, 2.79mmol) and K[HB(Pz)$_3$] (1.03g, 3.06mmol) in acetonitrile (45cm^3) was heated at 45° C for 0.3h before being cooled and poured into H_2O (60cm^3) containing concentrated

hydrochloric acid (1.5cm^3). No solid material was obtained and the reaction was abandoned.

2.7.6.1 Preparation of $Ph_4As[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$ (6)

To a stirred solution of $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (**1**) (0.60g, 1.67mmol) in methanol (5cm^3) was added a solution of $Ph_4AsCl.HCl.(H_2O)_2$ (0.43g, 0.88mmol) in aqueous 1M NaOH (10cm^3). An immediate yellow precipitate occurred and was filtered off after 1h stirring at room temperature, washed with water, dried and recrystallised from methanol containing a few drops of aqueous NaOH to give (**6**).

Yield: 0.41g (52%)

Infra-red: ν(C≡O) 1904, 1802cm^{-1}; ν(C-O) 1065cm^{-1}

NMR (^{1}H, $(CD_3)_2CO$, 270MHz): δ8.00-7.83 (20H, aromatics); 5.03(3H, s); 3.74(6H, s); 3.54 (4H, s); 3.37(6H, s); 2.78 (4H, s); 0.45 (4H, s)

NMR (^{13}C, $(CD_3)_2CO$, 68MHz): δ232.7 (C≡O); 134.8-131.3 (aromatics); 81.0 (O-CH_3); 80.5 ($CH_2C(CH_2OCH_3)CH_2$); 70.1 ($CH_2C(CH_2OCH_3)CH_2$); 61.2 ($CH_2C(CH_2OMe)CH_2$); 56.7 (O-CH_3); 53.9 ($CH_2C(CH_2OCH_3)CH_2$)

Microanalysis: Found; C, 51.7; H, 4.99; N, 0%. Calculated for $C_{41}H_{47}AsMo_2O_9$; C, 51.80; H, 4.98; N, 0%

2.7.6.2 Attempted preparation of

$Ph_4As[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OEt)CH_2\}_2(\mu\text{-}OEt)_3]$ (7)

The above procedure for complex (6) was repeated with ethanol as the reaction and (with a few drops of aqueous 1M NaOH) the recrystallisation solvent. From the spectral and analytical data, particularly the very complex ^1H NMR data obtained, it appears that a mixture of complexes was formed. Similar mixtures were also obtained on repeating the above.

Yield: (0.21g, 25%)

Infra-red: $\nu(C\equiv O)$ 1906, 1794cm^{-1}; $\nu(C\text{-}O)$ 1107, 1080, 1061cm^{-1}

NMR (^1H, $(CD_3)_2CO$, 270MHz): δ7.97-7.85 (20H, m); 5.05 (~1H, m); 3.80 (~2H, m); 3.72 (~1H, m); 3.58 (~4H, m); 2.90 (~3H, m); 2.77 (~4H, m); 2.04 (~2H, m); 1.80 (~1H, m); 1.45 (~2H, br s); 1.28 (~2H, t, J~7Hz); 1.18 (~6H, t, J=6.96Hz); 0.33 (4H, s)

NMR (^{13}C, $(CD_3)_2CO$, 68MHz): 135.5-132.0 (aromatics); 80.8, 78.6, 65.2, 65.1, 55.4, 15.9

(according to a 135 DEPT spectrum the peak at δ80.8 is a quaternary carbon; the peak at δ15.9 relates to a CH_3 group(s) whilst all the other peaks correspond to CH_2 moieties)

Microanalysis: Found; C, 51.2; H, 5.30; N, 0.12%. Calculated for $C_{46}H_{57}AsMo_2O_9$; C, 54.13; H, 5.63; N, 0%

2.7.6.3 Attempted preparation of

$Ph_4As[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OH)CH_2\}_2(\mu\text{-}(OH)_3)]$ (8)

Repeated as above with H_2O as the reaction solvent. The yellow precipitate recovered from the reaction could not be recrystallised from H_2O and further attempts at

purification appeared to lead to decomposition of the product. The infra-red data below therefore refers to the crude material.

Infra-red: ν(O-H) 3393cm^{-1}; ν(C≡O) 1898, 1784cm^{-1}

2.7.6.4 Preparation of $Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$ (9)

Repeated as for complex (**6**) but employing Et_4NCl instead of Ph_4AsCl. Recrystallisation from methanol containing a few drops of aqueous 1M NaOH yielded crystals suitable for an X-ray crystallographic study (see **Appendix 1**). This reaction was sensitive to the water content of the reaction mixture and yielded either an anhydrous product or a hydrated product.

Infra-red: ν(O-H) 3317cm^{-1}; ν(C≡O) 1924, 1904, 1790cm^{-1}; ν(C-O) 1055cm^{-1}

NMR (^{1}H, $CDCl_3$, 270MHz): δ5.05 (3H, s); 3.76 (6H, s); 3.58 (4H, s); 3.50 (6H, s); 3.25 (8H, q, J=7.3Hz); 2.93 (4H, s); 1.37 (12H, tt, J=1.8, 7.3Hz); 0.63 (4H, s)

NMR (^{13}C, $CDCl_3$, 68MHz): δ233.21 (C≡O); 81.02 (O-CH_3); 80.65 ($CH_2C(CH_2OMe)CH_2$); 70.43 ($CH_2C(CH_2OCH_3)CH_2$); 61.61 ($CH_2C(CH_2OMe)CH_2$); 57.92 (CH_3CH_2N); 54.28 ($CH_2C(CH_2OCH_3)CH_2$); 52.63 (O-CH_3); 7.49 (CH_3CH_2N) (assignments were confirmed by a 135DEPT spectrum)

Microanalysis: Found; C, 40.1; H, 6.36; N, 1.87%. Calculated for $C_{25}H_{47}Mo_2NO_9.2H_2O$; C, 40.93; H, 7.01; N, 1.91%

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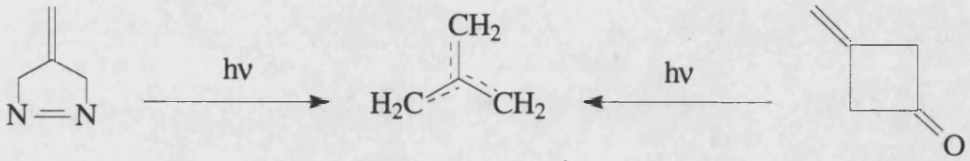
SECTION 3

TRANSITION METAL η^4-TRIMETHYLENEMETHANE COMPLEXES

3 TRANSITION METAL η^4-TRIMETHYLENEMETHANE COMPLEXES

The first trimethylenemethane metal complex to be synthesised, $[Fe(CO)_3\{\eta^4\text{-}C(CH_2)_3\}]$ (**I**), was reported in 1966 by Emerson *et al*[1] from the reaction between $[Fe_2(CO)_9]$ or $Na_2[Fe(CO)_4]$ and 3-chloro-2-chloromethylpropene (**II**). Complex (**I**) is stable at room temperature, in contrast to the uncomplexed, highly reactive triplet diradical trimethylenemethane[2-5] (**III**) which is only stable at -185°C (**Scheme 3.1**).

Scheme 3.1

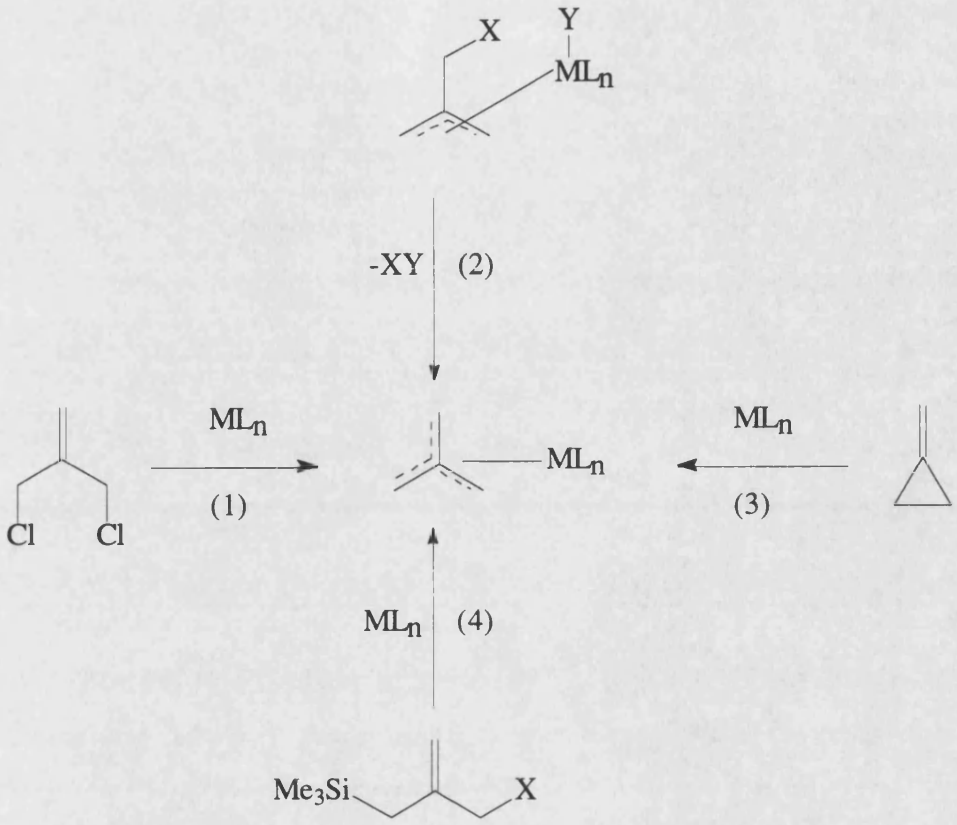


(**III**) stable at -185°C

Subsequently many other trimethylenemethane metal complexes have been synthesised and their reactivity, structure, bonding and synthetic utility extensively examined[6].

The methods of preparation of these complexes generally fall into one of the four routes summarised in **Scheme 3.2** which are discussed in more detail below.

Scheme 3.2

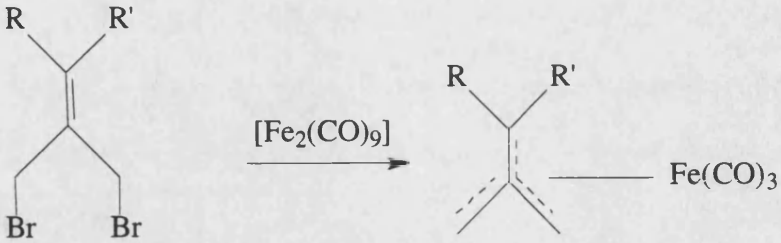


3.1 Methods of Preparation of Trimethylenemethane Complexes

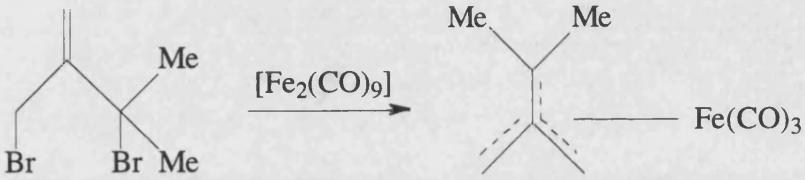
3.1.1 By dehalogenation of α, α'-dihalosubstituted alkene precursors

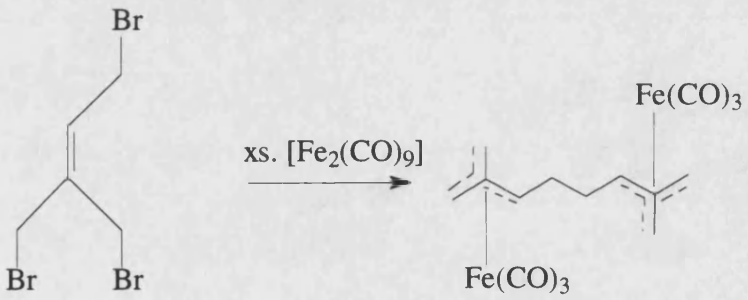
Several substituted trimethylenemethane-iron complexes have been prepared[1,7-10] in a similar manner to that of complex (**I**), utilising $[Fe_2(CO)_9]$ or $[FeCl_2(P)_2]P$ (P=PMe_3 or PMe_2Ph) and various substituted derivatives of (**II**) (**Scheme 3.1.1**).

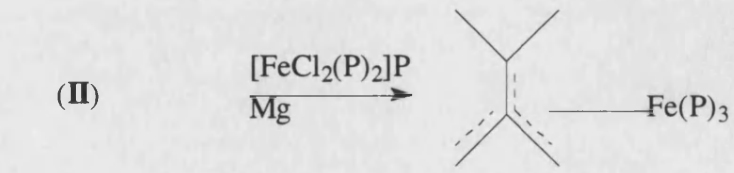
Scheme 3.1.1



R=H; R'=Ph, CO_2Me, CH(Me)(OAc); $R=R'=CO_2Et$







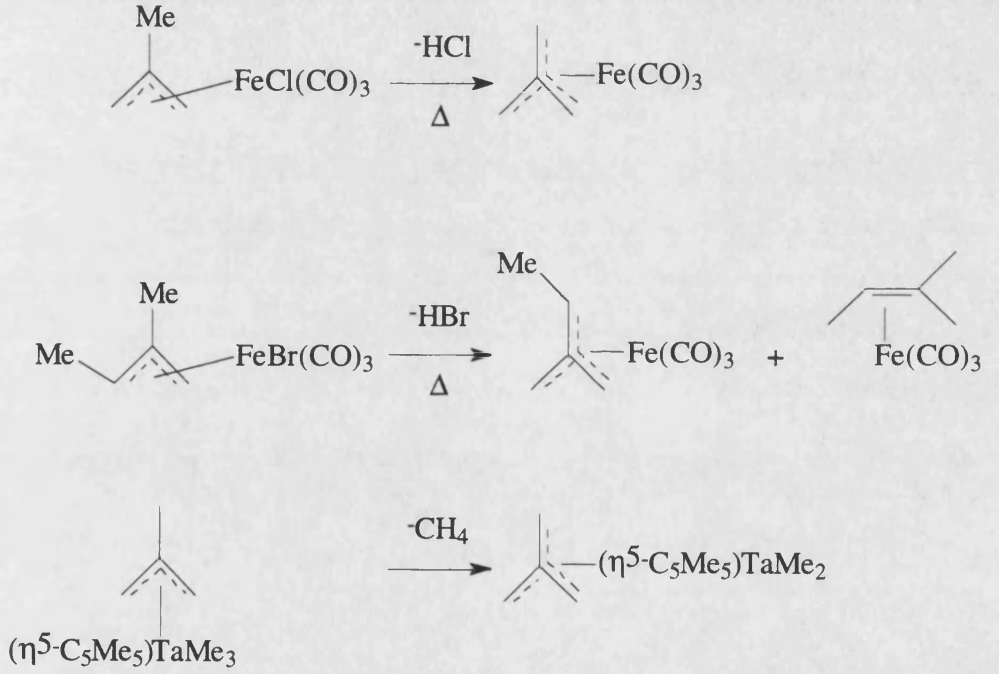
P=PMe_3 or PMe_2Ph

In addition the corresponding Group VI trimethylenemethane complexes $[M(CO)_4\{\eta^4\text{-}C(CH_2)_3\}]$ (M=Mo, Cr) have been prepared[8] by the reaction of (**II**) with $[Mo(CO)_5]^{2-}$ and $[Cr(CO)_6]$ respectively.

3.1.2 By thermal extrusion of simple molecules from η^3-allyl complexes

An alternative route to complex (**I**), involving the thermal elimination of HCl from the iron η^3-allyl complex $[Fe(CO)_3Cl\{\eta^3\text{-}CH_2C(Me)CH_2\}]$ has been employed by Emerson[7, 11]. Simple molecules such as HBr and CH_4 have also been thermally eliminated from other metal η^3-allyl complexes leading to the formation of the corresponding trimethylenemethane complexes[7,12] (**Scheme 3.1.2**).

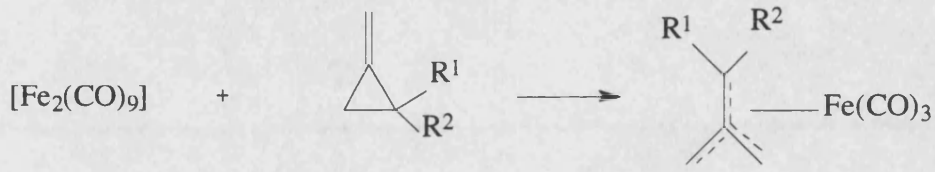
Scheme 3.1.2



3.1.3 By ring opening of alkylidenecyclopropanes

A range of iron trimethylenemethane complexes have been synthesised[13,14] by utilising the ring-opening reactions of 2-substituted methylenecyclopropanes with $[Fe_2(CO)_9]$ (**Scheme 3.1.3**).

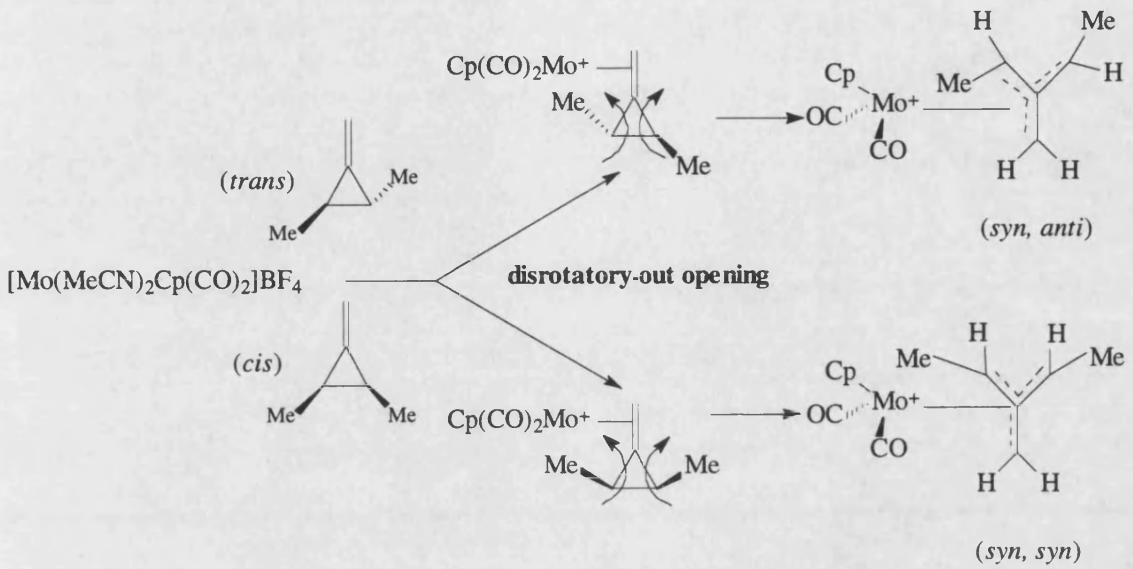
Scheme 3.1.3



R^1=H, R^2=Ph, $CH=CH_2$
R^1=Me, R^2=Ph
R^1=R^2=Ph

Stereospecific deuterium labelling experiments have shown that the ring-opening of 2-phenylmethylenecyclopropane, giving $[Fe(CO)_3\{\eta^4\text{-}C(CH_2)_2CHPh\}]$, occurs by a specifically disrotatory mode as predicted by FMO considerations[15-18]. The reactions of *cis*- and *trans*-2,3-dimethylmethylenecyclopropane in the presence of $[CpMo(NCMe)_2(CO)_2][BF_4]$ have also been shown[19,20] to follow a specifically disrotatory-out ring-opening mechanism as verified by the formation of the *syn*, *syn* and *syn, anti*-dimethyltrimethylenemethane complexes respectively (**Scheme 3.1.4**).

Scheme 3.1.4



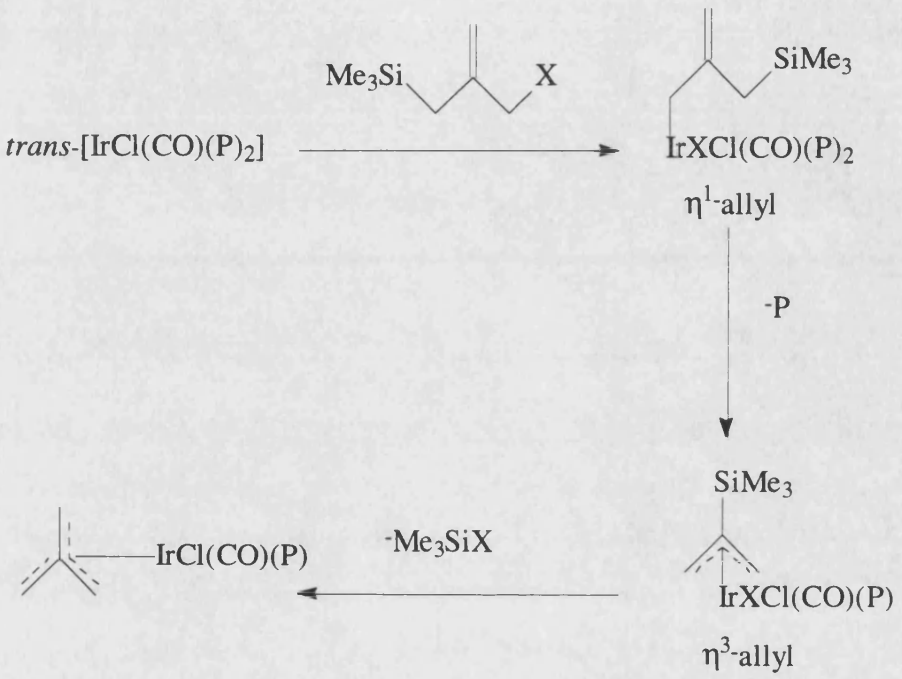
3.1.4 By elimination of Me_3SiX (X=OAc, Cl, OSO_2Me) from functionalised allyl silanes

The reaction between a Pd(0) catalyst $[Pd(PPh_3)_4]$ and $Me_3SiCH_2C(CH_2X)=CH_2$ (X=acetate) results in the formation of highly reactive $[Pd(PPh_3)_2\{\eta^3\text{-}C(CH_2)_3\}]$ *via* the elimination of trimethylsilyl acetate. This intermediate has been employed by Trost and Chan for the cycloaddition of the trimethylenemethane fragment with alkenes[21,22].

By a similar method a range of iridium, osmium, rhodium and ruthenium trimethylenemethane complexes have been prepared *via* the reaction of sulphonate (or chloride) functionalised allyl silanes with low valent phosphine or arsine derivatives of these metals[23-27]. The allyl silane initially undergoes oxidative addition to the metal, giving an η^1-allyl which rearranges to an η^3-allyl intermediate. Subsequent elimination of

the poorly coordinating methylsulphonate and desilylation of the η^3-allyl intermediate leads to the η^4-trimethylenemethane complex. An example is shown below (**Scheme 3.1.5**).

Scheme 3.1.5



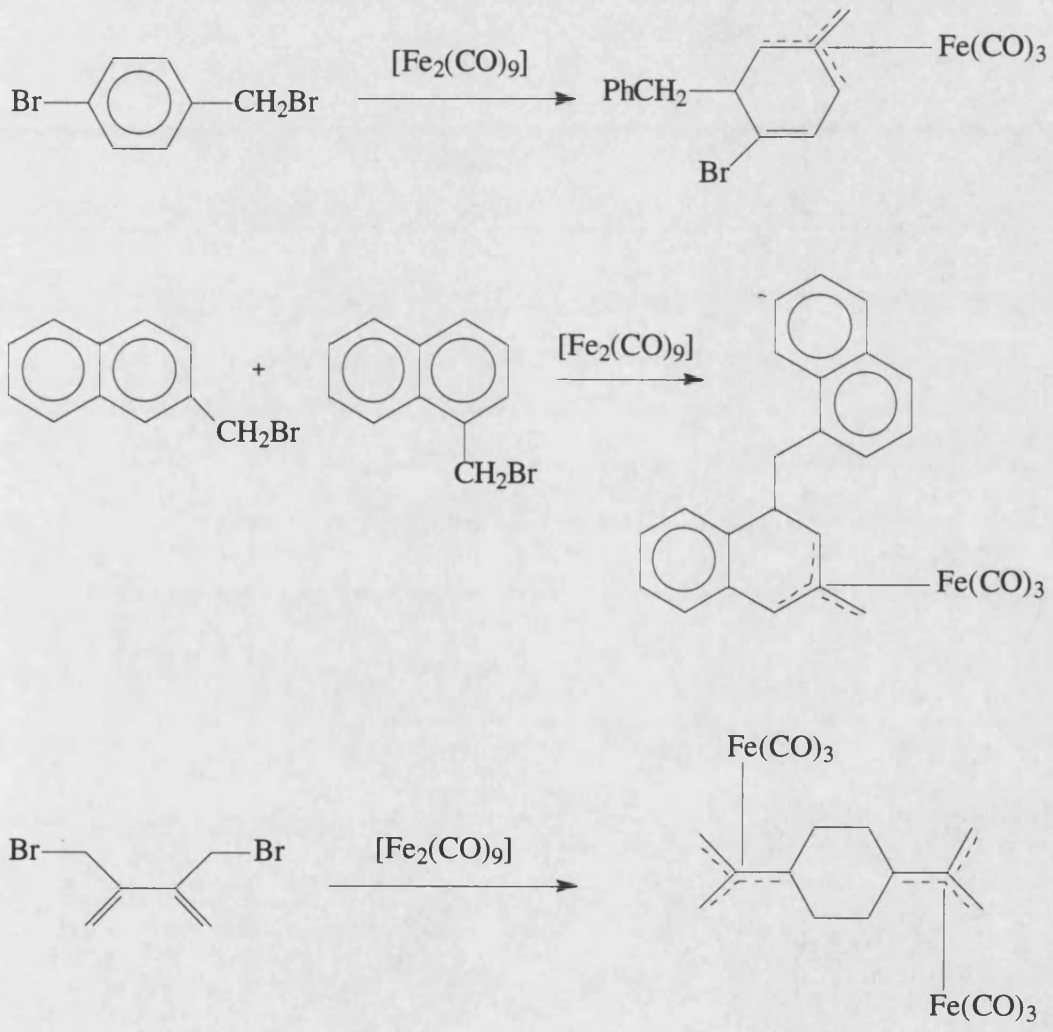
P=PPh_3; X=Cl or OSO_2Me

It is also possible to cleave the trimethylsilyl group from an η^3-allyl complex with fluoride ion, providing corroboration of the above mechanism[24].

3.1.5 Other routes

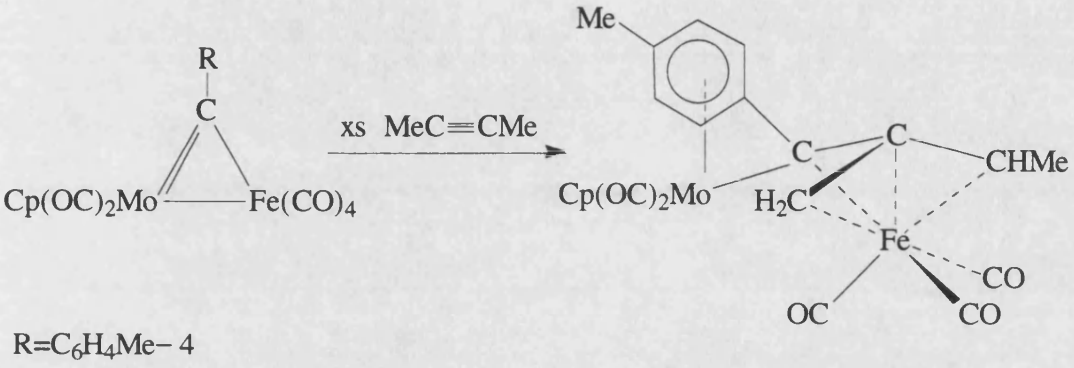
A further route into iron trimethylenemethane complexes is provided by the reaction of some bromomethylaryls with $[Fe_2(CO)_9]$. The reactions below (**Scheme 3.1.6**) are related in that they all involve a similar C-C coupling step[28-31].

Scheme 3.1.6



Other iron trimethylenemethane complexes can be prepared[32,33] from the reactions of $[Fe_2(CO)_9]$ with alkenes and 7-(hydroxymethyl)cycloheptatriene whilst the reaction of excess but-2-yne with a dinuclear μ-alkylidene complex leads to a novel metal-substituted iron trimethylenemethane complex[34] (**Scheme 3.1.7**).

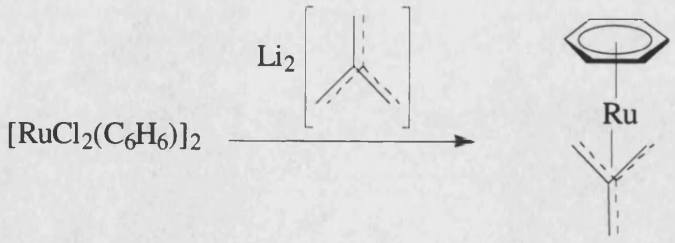
Scheme 3.1.7



R=C_6H_4Me-4

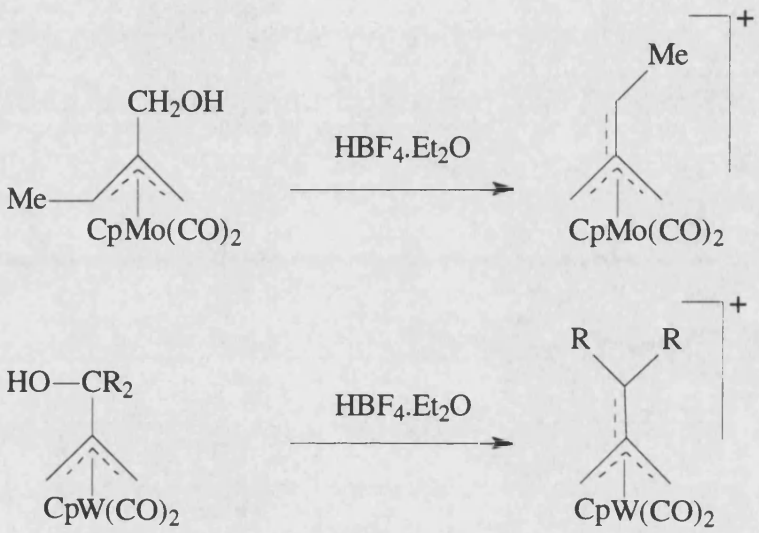
Ruthenium, iron, cobalt and rhodium trimethylenemethane complexes have been prepared *via* the lithium dianion of trimethylenemethane[35] (**Scheme 3.1.8**).

Scheme 3.1.8



The acid $HBF_4.Et_2O$ has been used to convert 2-hydroxymethylallyl complexes of molybdenum[36] and tungsten[37] into their respective η^4-trimethylenemethane complexes (**Scheme 3.1.9**).

Scheme 3.1.9



R=Me, Ph

3.2 Structure and Bonding in Transition Metal η^4-Trimethylenemethane Complexes

A number of single-crystal X-ray diffraction studies have been performed on iron trimethylenemethane complexes. For $[Fe(CO)_3\{\eta^4\text{-}C(CH_2)_3\}]$, it was found[38] that the carbonyl ligands and a trigonal-pyramidal trimethylenemethane ligand are in a staggered conformation about the metal. The Fe-C(central) bond length is 1.94(1)Å while the Fe-CH_2 distances are 2.12Å. Other iron trimethylenemethane complexes[28,39-44] and also the complexes[20,37] $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2\{\eta^4\text{-}C(CH_2)_3\}][BF_4]$, $[CpW(CO)_2\{\eta^4\text{-}CH_2C(CR_2)CH_2\}][BF_4]$ (R=Me, Ph) and[27] $[Ir(PPh_3)Cl(CO)\{\eta^4\text{-}C(CH_2)_3\}]$ have a similar arrangement of ligands about the metal with the trimethylenemethane ligand adopting an umbrella-like arrangement as shown in **Figure 3.2.1**.

Figure 3.2.1:-*Arrangement of ligands in transition metal η^4-trimethylenemethane complexes*

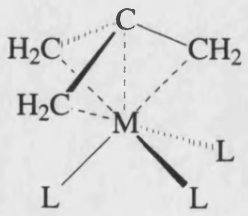
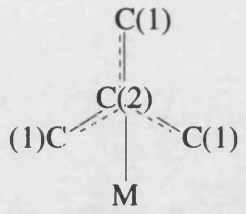


Table 3.2.1 overleaf lists bond lengths and angles for a few transition metal trimethylenemethane complexes.

Table 3.2.1



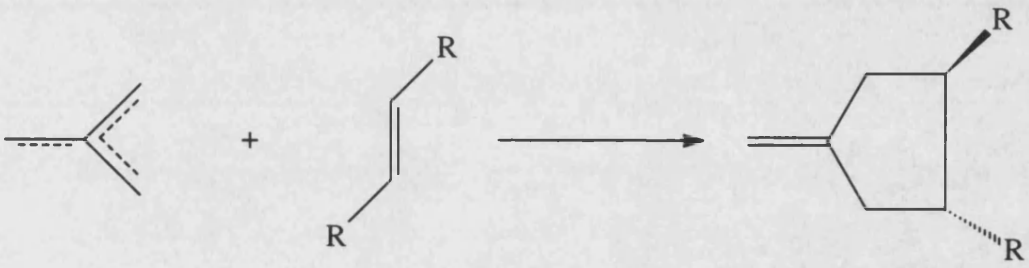
Complex	M-C(1) (Å)	M-C(2) (Å)	C(1)C(2) (Å)	θ^1 (°)	C(1)-C(2)-C(1) (°)	Ref
$[Fe(CO)_3\{\eta^4\text{-}C(CH_2)_3\}]$	2.123(5)	1.938(5)	1.437(3)	13.6(2)	114.6(2)	38
$[Ir(PPh_3)_2(CO)\{\eta^4\text{-}C(CH_2)_3\}][PF_6]$	2.288 2.201 2.173	2.053	—	14.0	—	27
$[(\eta^5\text{-}C_5Me_5)Mo(CO)_2\{\eta^4\text{-}C(CH_2)_3\}][BF_4]$	2.392(11) 2.358(9) 2.324(9)	2.213(10)	1.46(2) 1.40(2) 1.39(1)	14.6(5) 12.0(6) 10.6(6)	119(1) 115(1) 112(1)	20
$[CpW(CO_2)\{\eta^4\text{-}CH_2C(CMe_2)CH_2\}][BF_4]$	2.499(10) 2.338(13) 2.324(12)	2.189(12)	1.436(17) 1.433(19) 1.382(17)	13.3(7) 12.7(7) 4.3(8)	120.2(11) 120.0(12) 111.0(10)	37
$[CpW(CO_2)\{\eta^4\text{-}CH_2C(CPh_2)CH_2\}][BF_4]$	2.509(13) 2.340(15) 2.335(14)	2.175(15)	1.448(22) 1.454(19) 1.414(20)	13.4(9) 12.0(9) 5.0(9)	122.7(14) 115.8(13) 113.1(13)	37

1:- $\theta = 90 - \angle(M\text{-}C(1)\text{-}C(2))$

3.3 Reactivity of Transition Metal η^4-Trimethylenemethane Complexes

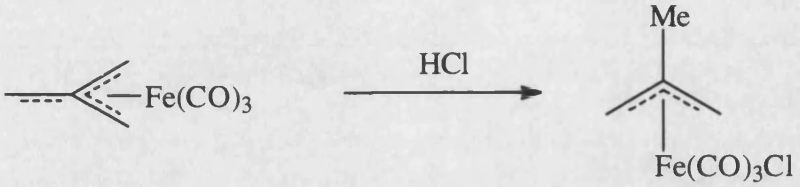
Transition metal η^4-trimethylenemethane complexes have been extensively employed in organic synthesis[21,22,45-59], particularly in the formation of five-membered ring systems (which are found in an abundance of natural products including prostaglandins) *via* a Diels-Alder ($4\pi+2\pi$) type reaction as shown in **Scheme 3.3.1**. As bond formations in such reactions occur almost simultaneously, stereochemical control can be exerted over the final product.

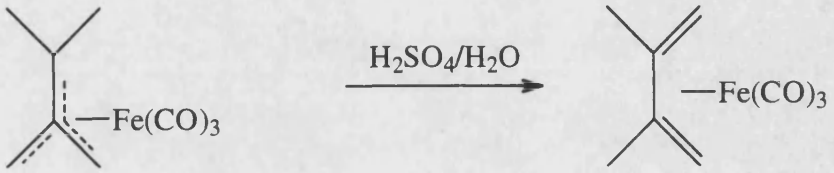
Scheme 3.3.1



Iron η^4-trimethylenemethane complexes have been found in a number of studies[7,9,60] to be susceptible to electrophilic attack as shown in **Scheme 3.3.2**.

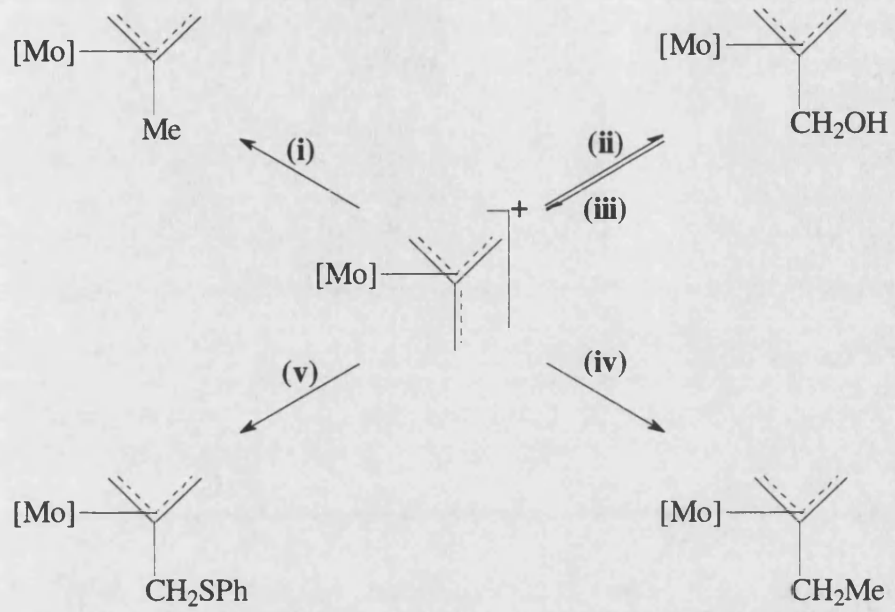
Scheme 3.3.2





The cationic molybdenum η^4-trimethylenemethane complex $[CpMo(CO)_2\{\eta^4\text{-}C(CH_2)_3\}][BF_4]$ (**a**), the first cationic η^4-trimethylenemethane complex to be prepared, was found to react with a range of nucleophiles as shown in **Scheme 3.3.3**.

Scheme 3.3.3

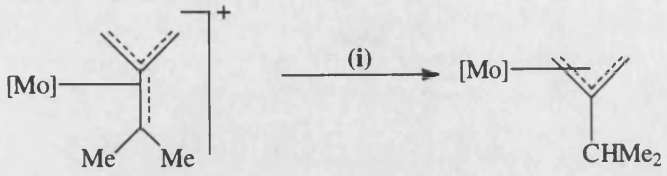


[Mo]=(η^5-C_5Me_5)Mo(CO)$_2$

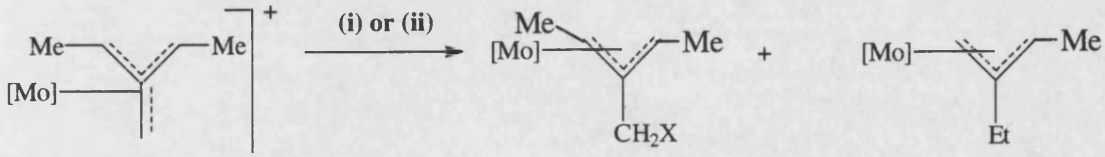
(i) BH_4^-; **(ii)** OH^-; **(iii)** HBF_4/$(EtOC)_2O$; **(iv)** $CuMe_2^-$; **(v)** SPh^-

The methyl-substituted analogues of complex (**a**), complexes (**b-d**), were also reacted with nucleophilic reagents, as shown in **Scheme 3.3.4**.

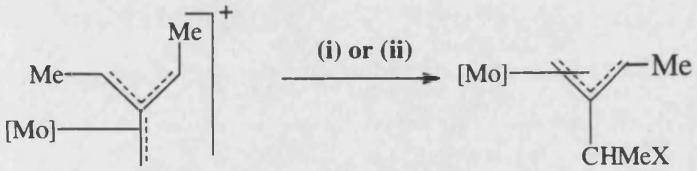
Scheme 3.3.4



Complex (b)



Complex (c) (with **(i)** only)



Complex (d)

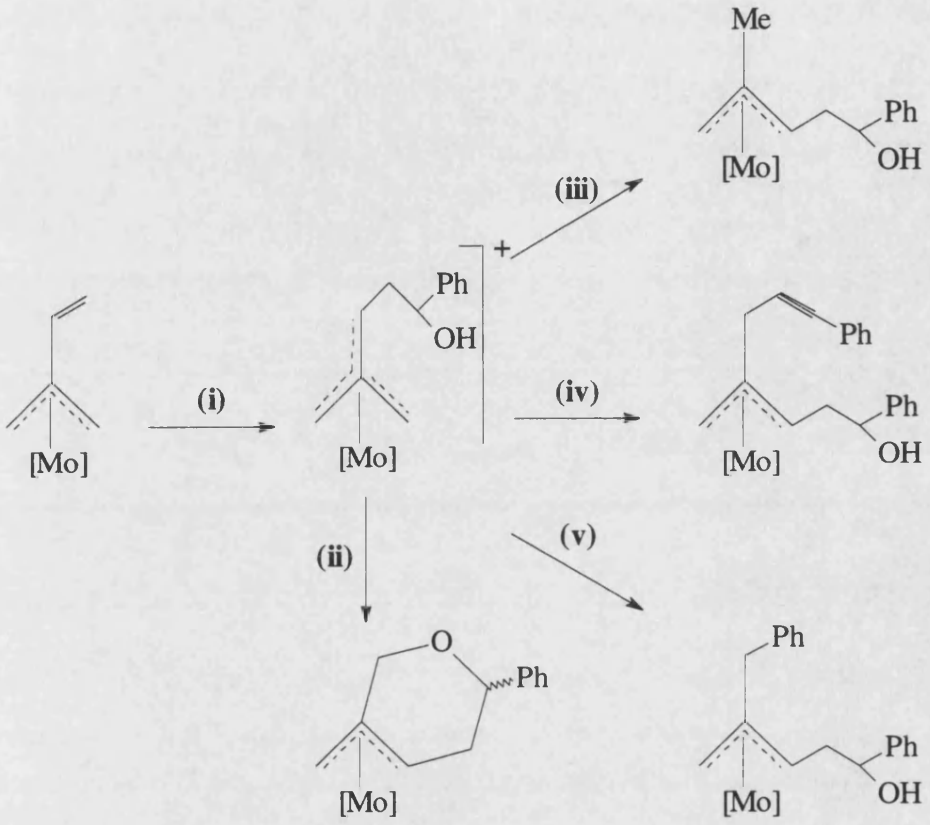
[Mo]=(η^5-C_5Me_5)Mo(CO)$_2$
(i): BH_4^-, X=H; **(ii)**: OH^-, X=OH

As shown above, complex (**b**) reacts with the BH_4^- anion to give exclusively a 2-isopropyl-substituted η^3-allylic complex. However, the same reagent attacks complex (**c**) at both the substituted and unsubstituted carbon atoms of the trimethylenemethane ligand. Attack by BH_4^- on complex (**d**) occurred regioselectively on a methyl-substituted carbon. Thus, it appears that a combination of steric and electronic control the position of nucleophilic attack in these complexes. This conclusion is supported by the results of

nucleophilic attack by OH^- which selectively occurs at the unsubstituted carbon of complex (**c**) and at a substituted carbon atom of complex (**d**).

More recently, Liu *et al*[36] have utilised the proposed intermediacy of a cationic molybdenum η^4-trimethylenemethane complex to prepare η^3-allyl complexes *via* reaction with nucleophiles as shown in **Scheme 3.3.5**. Subsequent decomplexation yielded olefins.

Scheme 3.3.5

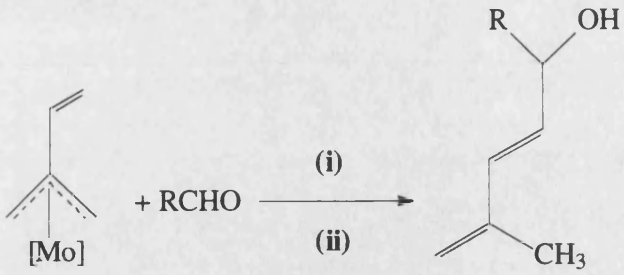


[Mo]=$CpMo(CO)_2$

(i) $PhCHO/BF_3.Et_2O$; **(ii)** Na_2CO_3; **(iii)** $NaBH_3CN$; **(iv)** $(PhC{=}C)_2CuLi$; **(v)** Ph_2CuLi

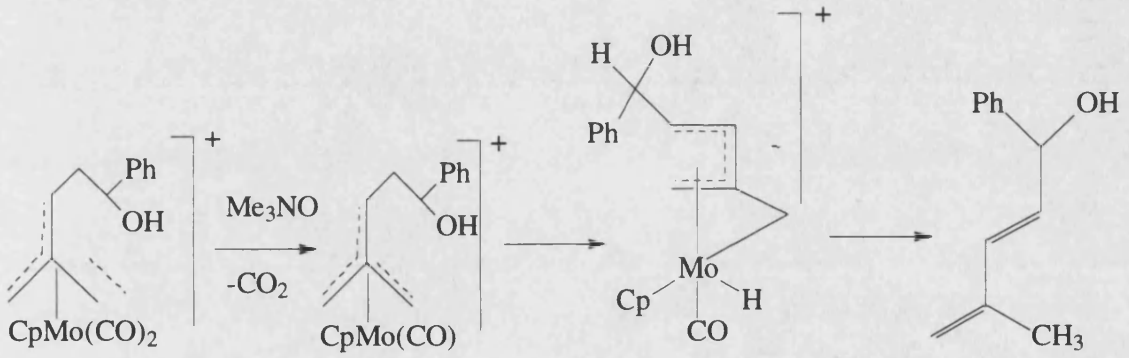
A range of substituted 1,3-dienes were also prepared by the reaction shown in **Scheme 3.3.6** (along with the likely mechanism). Thus, $[CpMo(CO)_2\{\eta^4\text{-}MeCHC(CH_2)_2\}][BF_4]$ may be considered to have the same functional equivalence as a 3-methyl-1,3-butadienyl-1-yl anion.

Scheme 3.3.6



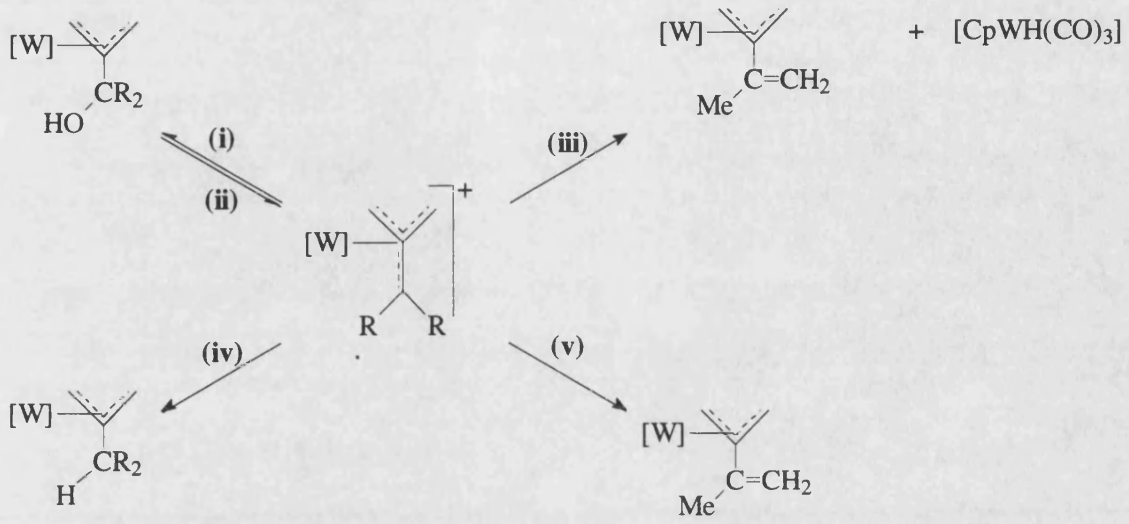
[Mo]=$CpMo(CO)_2$
R=Ph, $PhCH_2$, Me_2CH, t-C_4H_9, Me_2CHCH_2
(i) $BF_3.Et_2O$; **(ii)** Me_3NO

Proposed mechanism



Lin *et al*[37] have reported that the cationic tungsten η^4-trimethylenemethane complex $[CpW(CO)_2\{\eta^4\text{-}C(CR_2)_3\}]^+$ (R=Me, Ph) reacts with nucleophiles at the substituted terminal carbon atom as shown in **Scheme 3.3.7**.

Scheme 3.3.7



[W]=CpW(CO)$_2$

(i) NaOH; **(ii)** H$^+$; **(iii)** CpW(CO)$_3^-$, R=Me; **(iv)** $NaBH_4$; **(v)** MeLi, R=Me

It was also reported that weak bases such as amine and phosphine (as well as methyllithium) deprotonate the above complex (R=Me), thus generating β-substituted η^3-allylic complexes.

3.4 Attempts To Prepare η^4-Trimethylenemethane Complexes

To date several examples of η^4-trimethylenemethane complexes containing the $CpMo(CO)_2$ fragment have been synthesised and their characterisation reported in the literature. However, as yet none of the analogous and isoelectronic complexes of the type $[MoXL_2(CO)_2\{\eta^4\text{-}C(CH_2)_3\}]^+$ (L_2=bidentate or two monodentates, X=halide or trifluoroacetate) have been prepared. The discussion below concerns the attempts made to synthesise such η^4-trimethylenemethane derivatives from the complexes prepared earlier as outlined in **Section 2.6.**

The following routes, some of which have been successfully employed previously upon other η^3-allyl containing complexes (as discussed in **Section 3.1**), were attempted:-

(i) Abstraction of Cl^- from $[MoClL_2(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (L_2=$(MeCN)_2$, bipy (complexes (**1**) and (**3**) respectively),

(ii) Elimination of MeOH from complex (**6**) $Ph_4As[Mo_2(\mu\text{-}OMe_3)(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2]$ following protonation by a strong acid,

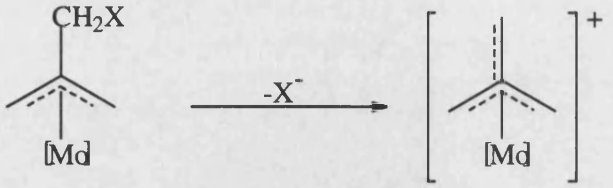
(iii) Removal of a proton from $[Mo(bpma)(CO)_2(\eta^3\text{-}2\text{-}C_3H_4Me)][PF_6]$ (**11**) by treatment with a strong base,

(iv) Thermal elimination of HCl from $[MoCl(bipy)(CO)_2(\eta^3\text{-}2\text{-}C_3H_4Me)]$ (**12**).

As shown in **Scheme 3.4.1**, routes **(i)** and **(ii)** would lead to cationic η^4-trimethylenemethane complexes whilst routes **(iii)** and **(iv)** would produce neutral derivatives.

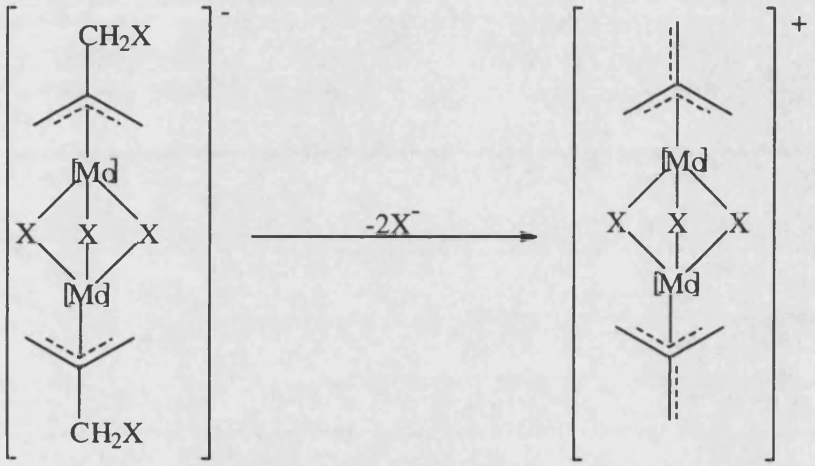
Scheme 3.4.1

Route (i)



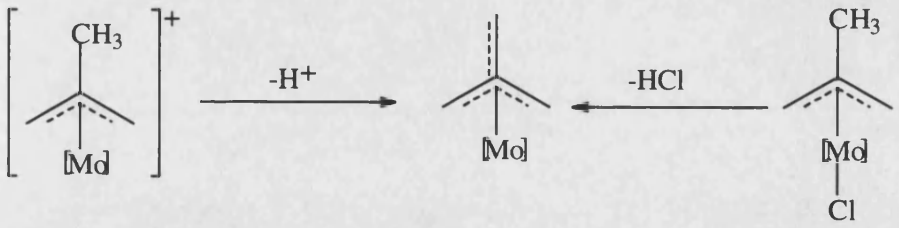
Complex (**1**) and (**3**): [Mo]=$MoClL_2(CO)_2$; L_2=$(MeCN)_2$ (**1**); L_2=bipy (**3**); X=Cl

Route (ii)



Complex (**6**): [Mo]=$Mo(CO)_2$; X=OMe

Route (iii) **Route (iv)**



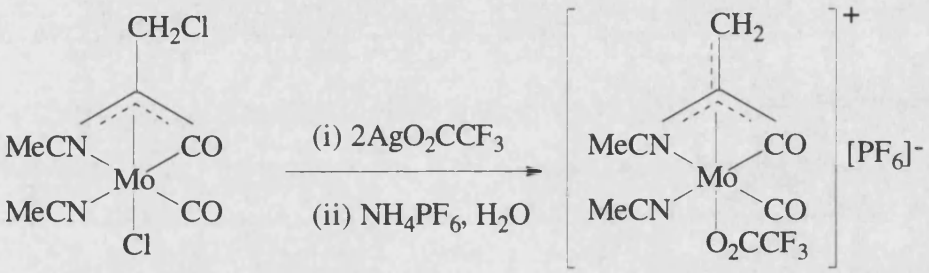
Complex (**11**): [Mo]=Mo(bpma)$(CO)_2$

Complex (**12**): [Mo]=Mo(bipy)(CO)

3.4.1 Reaction of [MoCl(MeCN)$_2$(CO)$_2${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (1) with silver trifluoroacetate

It was hoped that the reaction of [MoCl(MeCN)$_2$(CO)$_2${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (**1**) with a silver ion would result in the abstraction of a chloride ion from the -CH$_2$Cl moiety attached to the allyl group in (**1**), thus leading to the generation of an η^4-trimethylenemethane cation with silver chloride as an easily removed byproduct (**Scheme 3.4.2**).

Scheme 3.4.2



Complex (1)

As the chloride ion attached to the metal would also be removed, an aqueous solution of complex (**1**) was treated with 2 equivalents of silver trifluoroacetate. A white precipitate, presumed to be silver chloride, formed immediately and was filtered off and ammonium hexafluorophosphate added to provide a counter-ion for the expected cationic product. No precipitate was observed at this stage and despite reducing the solvent volume and refrigeration at 3°C, no solid product could be obtained from the reaction mixture despite further evaporation of the orange reaction solvent which appeared to cause the decomposition of any material contained in solution. Repeating this reaction in

acetonitrile, which is a less polar solvent and would thus be less likely to solvate any ionic products, also failed to yield the required product.

It is possible that the initial precipitate of silver chloride is caused by the abstraction of the chloride ion attached to the metal, and that the -CH_2Cl moiety is converted to a $CH_2O_2CCF_3$ group, *ie* $[Mo(O_2CCF_3)(MeCN)_2\{\eta^3\text{-}CH_2C(CH_2O_2CCF_3)CH_2\}]$ is formed. The resulting trifluoroacetate-substituted product would be more soluble than the chloride-substituted complex (**1**), as observed in other similar systems where trifluoroacetate is used as a replacement for a chloride ion attached to the metal, thus accounting for the difficulties in isolating a solid product.

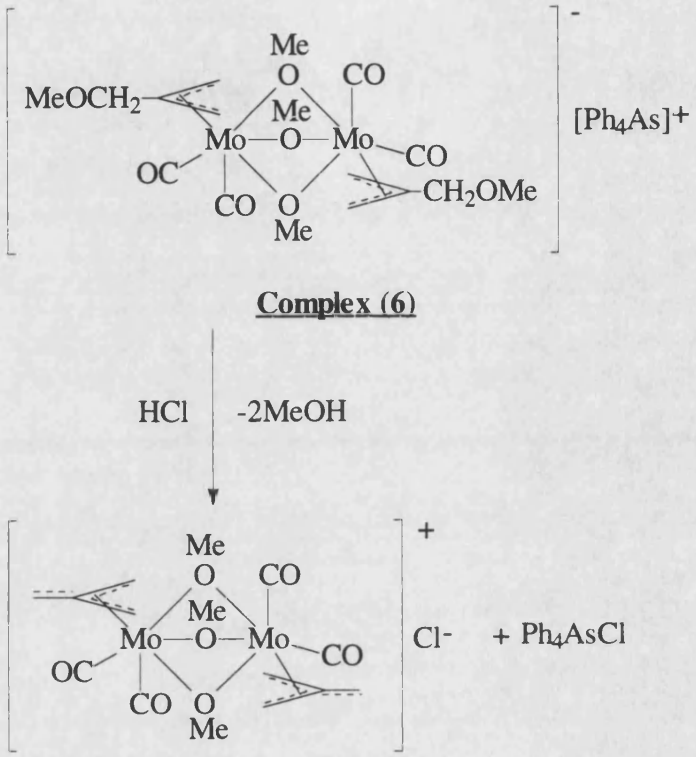
3.4.2 Reaction of $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (3) with silver trifluoroacetate

Complex (**3**) was treated with one equivalent each of sodium trifluoroacetate and silver trifluoroacetate whilst patially dissolved in acetone. After overnight stirring, evaporation of the reaction solvent *in vacuo* left a red tar which was redissolved in dichloromethane and treated with a few drops of cyclohexane. Refrigeration led to the precipitation of a small amount of a red solid which possessed two carbonyl bands in it's infra-red spectrum centred at 1946 and 1856cm^{-1}, as well as bands attributable to trifluoroacetate. However the ^1H NMR spectrum of this material proved to be very complex and the elemental analysis was not close to that expected, either for a trimethylenemethane complex or for the complex $[Mo(O_2CCF_3)(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CH_2O_2CCF_3)CH_2\}]$, and it appears that the reaction has led to the formation of a mixture of complexes. Further treatment of the mother liquors remaining after filtration failed to yield any more solid material and given the poor yield, the reaction was not proceeded with any further.

3.4.3 Reaction of $Ph_4As[Mo_2(\mu\text{-}OMe)_3(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2]$ (6) with HCl gas

As shown in **Scheme 3.1.9**, $HBF_4.Et_2O$ has been used to protonate 2-hydroxymethylallyl molybdenum and tungsten complexes, which, following elimination of H_2O are converted to their respective η^4-trimethylenemethane analogues. In a similar fashion it was hoped that treatment of complex (**6**) with acids would lead to elimination of MeOH and formation of the η^4-trimethylenemethane derivative of (**6**). To this end, complex (**6**) was dissolved in dichloromethane and treated with hydrogen chloride gas. The reaction mixture was observed to change in colour from yellow to dark brown during the addition of the gas and an infra-red spectrum taken after 0.75h stirring at room temperature showed the presence of a dicarbonyl species with $\nu(C\equiv O)$ bands at 1946 and 1860cm^{-1}. As the infra-red spectrum of complex (**6**) contains two carbonyl bands centred at 1903 and 1804cm^{-1}, this upward shift in wavenumber is consistent with the presence in solution of a cationic derivative which, as shown in **Scheme 3.4.3,** would be expected to have been formed from (**6**).

Scheme 3.4.3



Addition of ether and overnight refrigeration of the reaction mixture yielded two crops of a dark brown solid. Both were found to be non-carbonyl containing and it appeared that the dicarbonyl species detected in solution had decomposed. Rather than repeating this reaction, in which it was difficult to determine accurately the amount of HCl gas added, the more easily handled concentrated hydrochloric acid was subsequently employed as the protonating agent.

3.4.4 Reaction of $Ph_4As[Mo_2(\mu\text{-}OMe)_3(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2]$ (6) with concentrated hydrochloric acid

Complex (**6**) was dissolved in acetone and a few drops of concentrated hydrochloric acid followed by two equivalents of an aqueous solution of ammonium hexafluorophosphate were added. It was hoped that, if a cationic η^4-trimethylenemethane dimer was formed, the PF_6^- would act as a suitable counter-ion, inducing precipitation and subsequent isolation of the desired complex. Following the addition of the acid, an infra-red spectrum of the reaction mixture was taken. The spectrum indicated the presence of a dicarbonyl species with two $\nu(C\equiv O)$ bands at 1939 and 1848cm^{-1}; no starting material remained. An off-white precipitate formed immediately upon the addition of the aqueous NH_4PF_6 solution due to formation of Ph_4AsPF_6. Diethyl ether was added to the dark yellow filtrate which was refrigerated. No precipitate occurred and the material was observed to decompose upon standing.

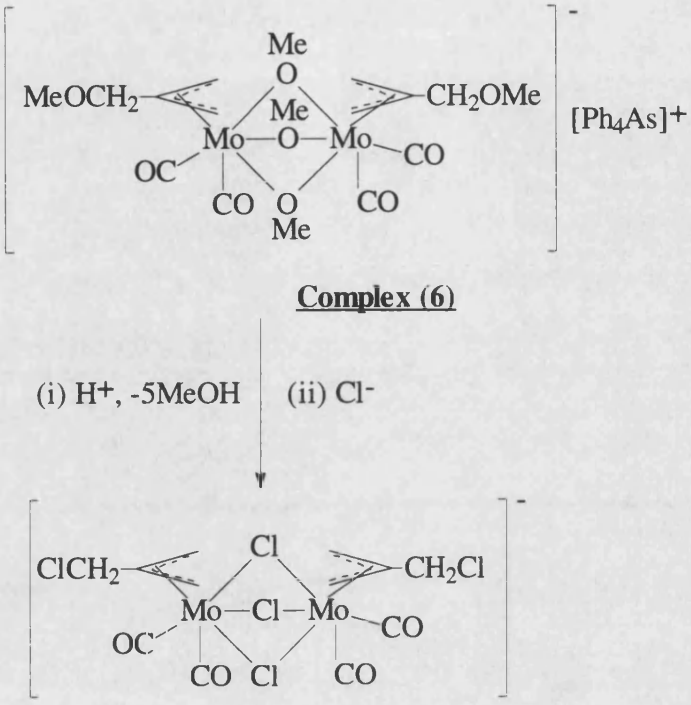
The above procedure was repeated and, after the initial off-white precipitate was filtered off, a further 2 equivalents of aqueous ammonium hexafluorophosphate solution were added. However, as with the previous reaction, no precipitate was forthcoming despite the addition of diethyl ether and refrigeration.

Several possibilities could account for the failure of the above reactions:-

(a) An η^4-trimethylenemethane complex could have been formed in solution but not have been sufficiently stable to be isolated. The carbonyl bands in the infra-red spectra taken of the various reaction solutions were consistently shifted upwards in wavenumber by about 40-50cm^{-1} with respect to complex (**6**). This would be expected if a cationic complex had been formed as shown in **Scheme 3.4.3**. However, there is no other evidence to support this theory and the following appears more plausible,

(b) It seems probable that not only was the $-CH_2OMe$ group protonated and MeOH eliminated, but that the bridging methoxy groups also reacted with acid. As the methoxy-bridged dimeric derivatives of complex (**6**) were originally prepared by reacting the tris-μ-chloro analogues with basic methanol, it is possible that the reverse is occurring here and the chloro-bridged dimers are formed in the reaction. It is also likely that any cationic η^4-trimethylenemethane complex formed would quickly react with the chloride ions present in solution, the product thus being $[Mo_2(\mu\text{-}Cl)_3(CO)_4\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}_2]^-$. Such a complex would be very soluble in the reaction solvents employed, acetone or dichloromethane, hence the difficulties encountered in isolating a solid product. It is also pertinent to note that the complex $[Mo_2(\mu\text{-}Cl)_3(CO)_4\{\eta^3\text{-}2\text{-}MeC_3H_4\}_2]^-$ has ν(C≡O) bands at 1940 and 1842cm^{-1} in its infra-red spectrum, a similar position to the bands observed in the infra-red spectra taken of the various reaction solutions. **Scheme 3.4.4** illustrates the proposed outcome of the reactions.

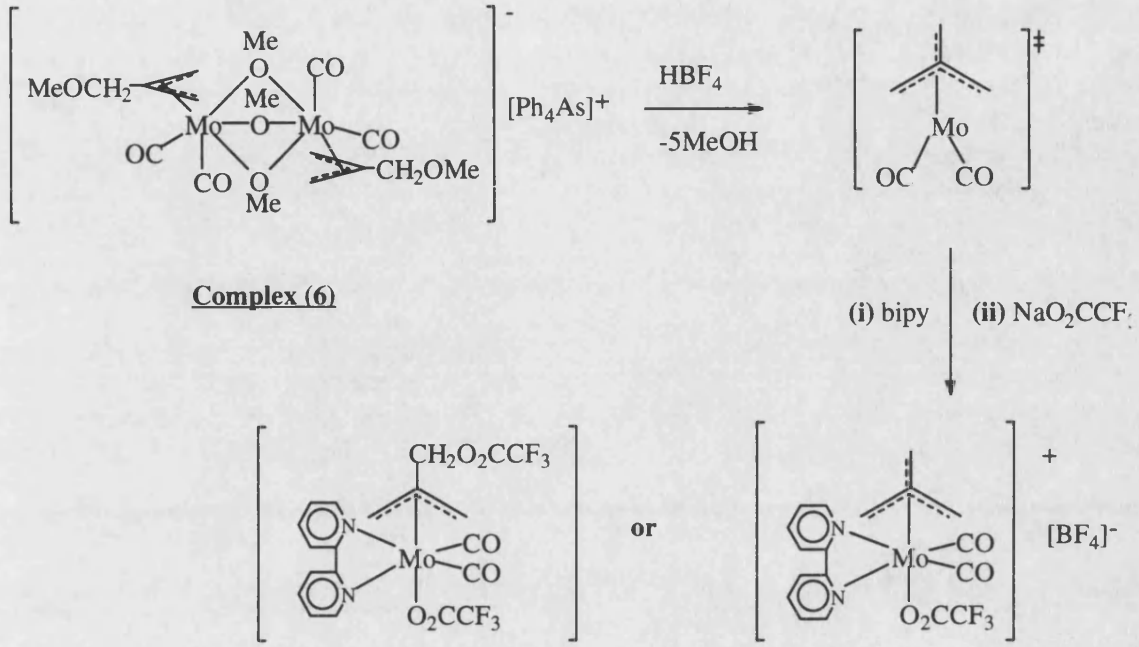
Scheme 3.4.4



3.4.5 Reaction of $Ph_4As[Mo_2(\mu\text{-}OMe)_3(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2]$ (6) with fluoroboric acid and 2,2'-bipyridyl

By reacting complex (**6**) with HBF_4 it was hoped that the methoxy-bridges would be broken as proposed above, and as the BF_4^- anion would be unlikely to act as a bridge itself, subsequent addition of 2,2'-bipyridyl and sodium trifluoroacetate would "trap" any resulting intermediate, as shown in **Scheme 3.4.5**.

Scheme 3.4.5



Complex (6)

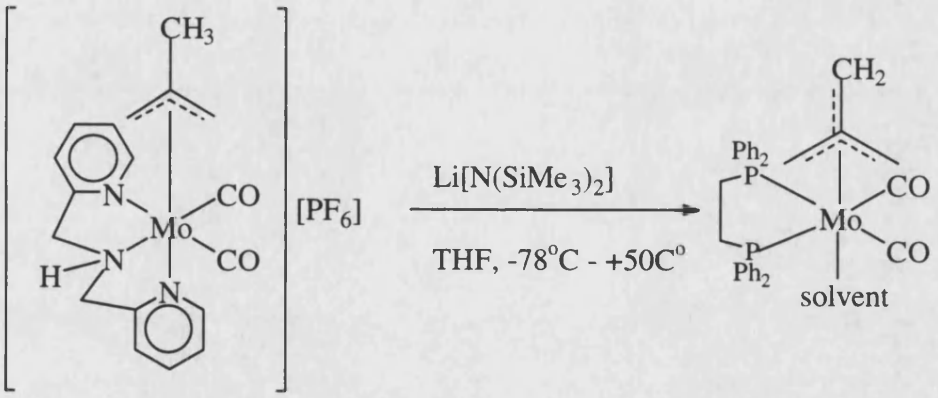
Accordingly, complex (**6**) was dissolved in acetone and treated with a few drops of an aqueous 50% solution of fluoroboric acid. After the resulting white precipitate (presumably of Ph_4AsBF_4) was filtered off, solutions of sodium trifluoroacetate and 2,2'-bipyridyl (both dissolved in acetone) were added dropwise to the yellow reaction filtrate. The reaction mixture darkened in colour to a deep red immediately on adding the 2,2'-bipyridyl solution. Addition of diethyl ether and overnight refrigeration induced the precipitation of a dark-red solid (**13**) which was isolated by filtration and dried under suction. The infra-red spectrum of complex (**13**) contained two ν(C≡O) bands centred at 1958 and 1892cm^{-1} along with peaks attributable to the bipyridyl ligand. A ν(C≡O) band was present at 1696cm^{-1}, indicating that the trifluoroacetate ligand had also been incorporated into the complex. The ^1H NMR spectrum of complex (**13**), obtained in CD_2Cl_2, contained a multiplet between δ8.82-7.42 with a relative intensity of 8. Singlet signals were also found at δ3.02, 2.94, 2.82, 1.53 and 1.31 with relative intensities of

1:1.7:1.3:1.2:1.2 respectively. This appears to indicate that complex (**13**) is in fact a mixture of at least two complexes. The elemental analysis obtained for (**13**) reinforces this view as it was not close to that expected and no reasonable formulation for a single complex could be made. Unfortunately, attempts to recrystallise the material obtained were not successful despite employing several different solvent systems.

3.4.6 Reaction of [Mo(bpma)(CO)$_2$(η^3-2-MeC$_3$H$_4$)][PF$_6$] (11) with lithium bis(trimethylsilyl)amide

By treating complex (**11**) with a strong base, it was hoped that a proton from the 2-methylallyl moiety could be remove, thus generating a complex which could then be ligated by a bidentate such as dppe to give a neutral η^4-trimethylenemethane complex as shown in **Scheme 3.4.6**.

Scheme 3.4.6



Complex (11)

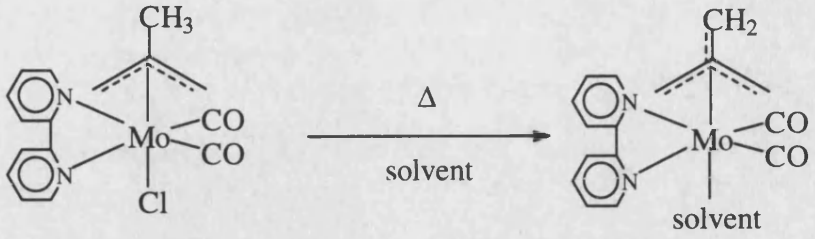
Accordingly, complex (**11**) was reacted with lithium bis(trimethylsilyl)amide in THF at -78°C, followed by the addition of a solution of dppe in THF. The resulting red

reaction mixture was then allowed to warm to room temperature at which point an infra-red spectrum taken showed the presence of several carbonyl-containing species including the starting material. In order to drive the reaction towards the formation of a single complex, the reaction mixture was then heated to 45-50°C for 2h. An infra-red spectrum taken at this time was, however similar to that previously obtained. The reaction solvent was removed by evaporation under a rapid stream of dry, dinitrogen gas and the green residue thus obtained redissolved in dichloromethane. The addition of diethyl ether and overnight refrigeration resulted in the formation of a green precipitate which was a non-carbonyl containing species. It is likely that the strong base used induced the decomposition of complex (**11**), possibly by initial deprotonation of the bpma ligand leading to an unstable species which broke down under the reaction conditions employed.

3.4.7 Attempted thermal elimination of HCl from [MoCl(bipy)(CO)$_2$(η^3-2-MeC$_3$H$_4$)] (12)

In order to thermally eliminate HCl from complex (**12**), it was heated for 2.5-3 hours in refluxing toluene, toluene/pyridine and finally xylene/pyridine as shown in **Scheme 3.4.7**.

Scheme 3.4.7



Complex (12)

solvent=$PhCH_3$, $PhCH_3$/py or xylene/py

In each case however, only starting material was recovered after the reflux and there was no evidence for the presence of any other complex. Thus, it appears that complex (**12**) is extremely thermally stable.

3.4.8 Conclusions

No firm evidence was found in any of the above reactions to suggest that an η^4-trimethylenemethane complex had been formed. Unfortunately, time constraints prevented any further exploration of the above reactions by employing more rigorous reaction conditions (*ie* Schlenk techniques) or changing reaction conditions, reagents or solvents.

3.5 EXPERIMENTAL

3.5.1 Reaction of [MoCl(MeCN)$_2$(CO)$_2${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (1) with silver trifluoroacetate

To complex (**1**) (300mg, 0.84mmol) dissolved in water (5cm^3) was added, dropwise with stirring, a solution of silver trifluoroacetate (380mg, 1.72mmol) in water (2cm^3). A white precipitate formed immediately and, after stirring for 0.3h, the reaction mixture was filtered and a solution of ammonium hexafluorophosphate (150mg, 0.92mmol) in water (2cm^3) was added to the yellow filtrate. No precipitation was observed at this stage and reduction of the reaction solvent volume followed by refrigeration did not yield a solid product. On prolonged standing decomposition was observed to occur.

The above procedure was repeated employing acetonitrile as solvent but again no solid material could be obtained from the reaction mixture before decomposition occurred.

3.5.2 Reaction of [MoCl(bipy)(CO)$_2${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (3) with silver trifluoroacetate

To a stirred solution of sodium trifluoroacetate (180mg, 1.32mmol) dissolved in acetone (30cm^3), was added [MoCl(bipy)(CO)$_2${η^3-CH$_2$C(CH$_2$Cl)CH$_2$}] (0.50g, 1.15mmol) and, dropwise, a solution of silver trifluoroacetate (260mg, 1.17mmol) dissolved in acetone (2cm^3). After 22h at room temperature, the mixture was filtered, and the red filtrate reduced in volume *in vacuo* to ~10cm^3 and added to a stirred solution of diethyl ether (5cm^3) which caused the formation of a tar. The reaction liquors were then evaporated to dryness *in vacuo* and the resultant red tar redissolved in dichloromethane

($10cm^3$), a few drops of cyclohexane were then added which resulted in the formation of a red precipitate which was filtered off, washed with cyclohexane ($10cm^3$) and dried.

Yield=142mg

Infra-red: $\nu(C\equiv O)$ 1946, 1856cm^{-1}; $\nu(C=O)$ 1686cm^{-1}; $\nu(C\text{-}F)$ 1200, 1161, 1134cm^{-1}; $\nu(C\text{-}O)$ 1034cm^{-1}

NMR (^1H, CD_3COCD_3, 270MHz): very broad and complex; appears to be a mixture of complexes

Microanalysis: Found; C, 34.1; H, 2.38; N, 3.93%. Calculated for $C_{20}H_{14}F_6MoN_2O_6$; C, 42.33; H, 2.76; N, 5.49%

3.5.3 Reaction of $Ph_4As[Mo_2(\mu\text{-}OMe)_3(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}]$ (6) with HCl gas

To a stirred solution of complex (**6**) (0.50g, 0.53mmol) in dichloromethane ($10cm^3$) was added hydrogen chloride gas (20s burst). The reaction mixture darkened in colour and an infra-red spectrum taken at this stage showed a dicarbonyl product present in solution with $\nu(C\equiv O)$ modes at 1946 and 1860cm^{-1}. Diethyl ether ($5cm^3$) was added and the reaction mixture refrigerated overnight. Three crops of a brown solid were obtained by filtration. All were devoid of CO and the reaction was not proceeded with any further.

3.5.4 Reaction of $Ph_4As[Mo_2(\mu\text{-}OMe)_3(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2]$ (6) with concentrated hydrochloric acid

To a stirred solution of complex (**6**) (0.50g, 0.53mmol) dissolved in acetone ($5cm^3$) was added hydrochloric acid (3 drops). Infra-red spectra of the reaction mixture

taken at this point revealed two carbonyl bands centred at 1939 and 1848cm^{-1}. A solution of ammonium hexafluorophosphate (180mg, 1.10mmol) in water (1cm^3) was then added to the reaction mixture. The resulting off-white precipitate (believed to be Ph_4AsPF_6) was filtered off. Diethyl ether was then added to the reaction filtrate which was refrigerated. No solid precipitate was forthcoming even on prolonged standing.

The above procedure was repeated, but with the addition of a further two equivalents of ammonium hexafluorophosphate added after the initial precipitate (Ph_4AsPF_6) was filtered off. However, no further precipitate occurred upon the addition and further treatment of the reaction solution yielded no carbonyl containing products.

3.5.5 Reaction of $Ph_4As[Mo_2(\mu\text{-}OMe)_3(CO)_4\{\eta^3\text{-}CH_2C(CH_2OMe)CH_2\}_2]$ (6) with fluoroboric acid and 2,2'-bipyridyl

To complex (**6**) (350mg, 0.37mmol) dissolved in acetone (5cm^3) was added, dropwise with stirring, fluoroboric acid (4 drops of a 50% solution in water). A white precipitate so formed was filtered off and found by infra-red spectroscopy to be a non-carbonyl containing species. To the filtered reaction solution, under dry N_2, was added solutions of sodium trifluoroacetate (110mg, 0.81mmol) followed by 2,2'-bipyridyl (130mg, 0.83mmol), both dissolved in 1.5cm^3 of acetone. The reaction solution darkened to a deep red colour upon adding the 2,2'-bipyridyl. Addition of diethyl ether (3cm^3) and refrigeration of the reaction mixture caused the precipitation of a dark-red solid (**13**) which was filtered off, washed with diethyl ether (5cm^3) and dried.

Yield=228mg

Infra-red: ν(C≡O) 1958, 1892cm^{-1}; ν(C=O) 1696cm^{-1}

NMR (^{1}H, $CDCl_3$, 270MHz): δ8.82-7.42 (9H, m); 3.02 (~1.2H, s); 2.94 (2H, s); 2.82 (~1.3H, s); 1.53 (~1.6H, s); 1.31 (~1.3H, s)

Microanalysis: Found; C, 46.4; H, 3.39; N, 4.61%. Calculated for $C_{18}H_{14}BF_7MoN_2O_4$; C, 38.46, H, 2.51; N, 4.98%

3.5.6 Reaction of [Mo(bpma)(CO)$_2$(η^3-2-MeC$_3$H$_4$)][PF$_6$] (11) with lithium bis(trimethylsilyl)amide

To complex (**11**) (0.40g, 0.73mmol) in THF (15cm^3) at -78°C was added dropwise with stirring lithium bis(trimethylsilyl)amide (0.75cm^3 of 1M solution in THF, 0.75mmol) followed by 1,2-bis(diphenylphosphino)ethane (0.32g, 0.80mmol) dropwise as a solution in THF (10cm^3). The resulting red reaction mixture was then allowed to warm to room temperature at which point an infra-red spectrum was recorded which showed a mixture of carbonyl-containing species were present. The reaction mixture was then heated at 45-50°C for 2h. A solution infra-red spectrum taken at this stage was similar to the previous spectrum recorded before heating. The reaction solvent was then removed by evaporation under a stream of dry dinitrogen gas leaving a green solid residue which was redissolved in dichloromethane (10cm^3) and diethyl ether (5cm^3) added. A green non-carbonyl containing precipitate was obtained.

3.5.7 Attempted thermal elimination of HCl from complex (12), [MoCl(bipy)(CO)$_2$(η^3-2-MeC$_3$H$_4$)]

Complex (**12**) was heated under reflux in toluene, xylene or toluene containing a few drops of pyridine for 2.5-3h. In each case only starting material was obtained.

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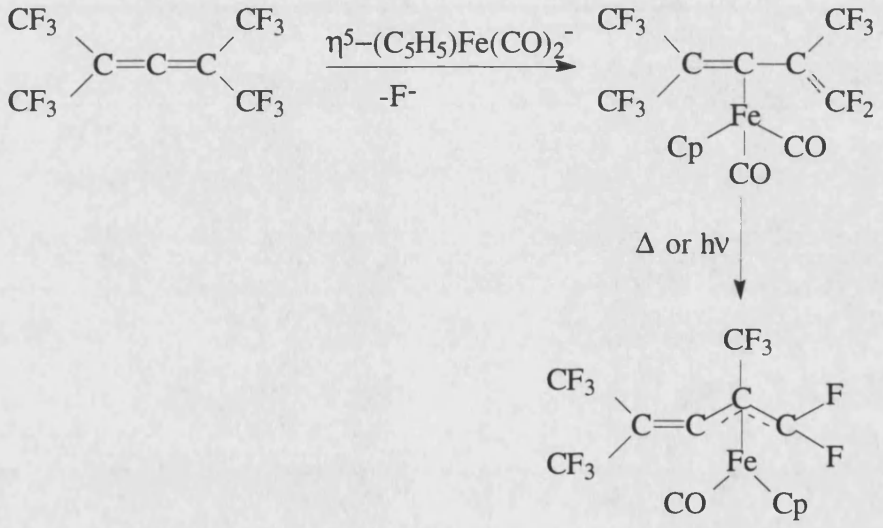
SECTION 4

TRANSITION METAL η^3-BUTADIENYL COMPLEXES

4 TRANSITION METAL η^3-BUTADIENYL COMPLEXES

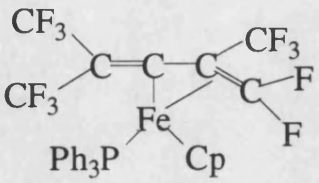
The first transition metal η^3-butadienyl complex, that of iron, was obtained in 1975 by Nesmeyanov and his co-workers[1,2] from the reaction of 1,1,3,3-tetrakis(trifluoromethyl)allene with the sodium salt of the carbonylate anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$, followed by heating or U.V. irradiation of the resulting σ-diene complex (**Scheme 4.1**).

Scheme 4.1



X-ray data obtained for the triphenylphosphine substituted derivative, $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)\{\eta^3\text{-}CF_2C(CF_3)C{=}C(CF_3)_2\}]$ confirmed the η^3-butadienyl structure, rather than the alternative σ, π-configuration (**Figure 4.1**).

Figure 4.1:- ***Alternative σ, π-configuration***



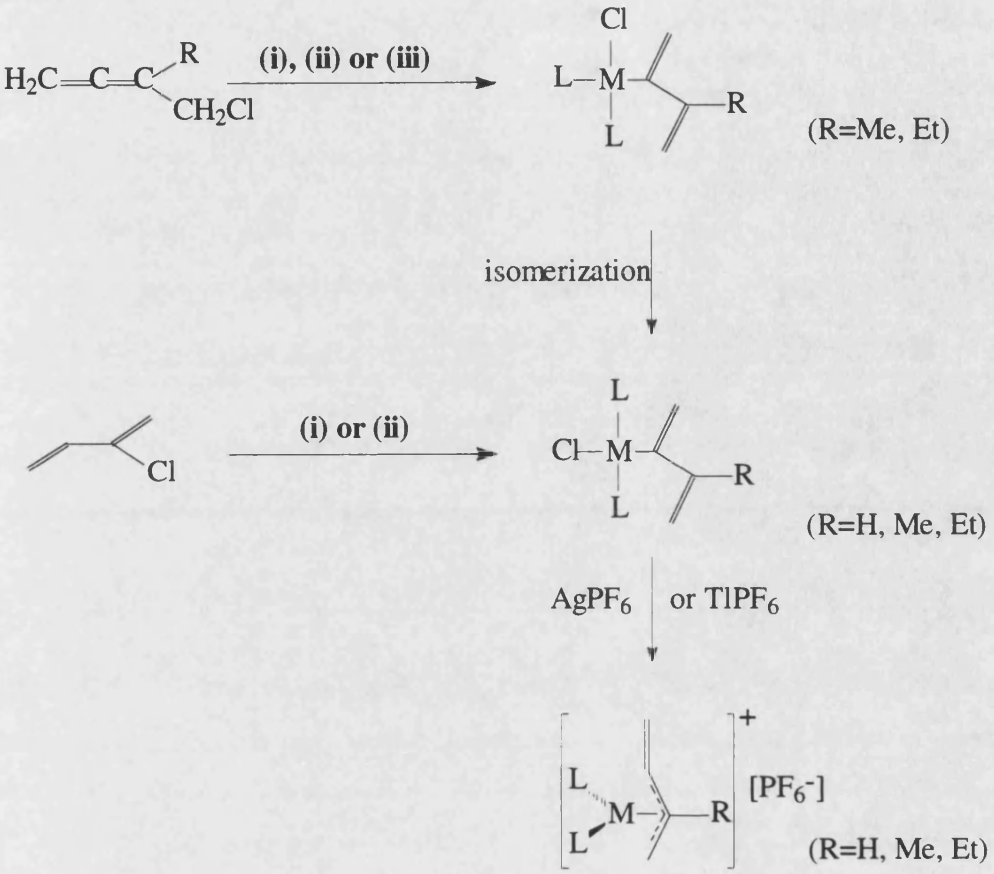
Subsequently a number of transition metal η^3-butadienyl complexes, both neutral and charged, have been prepared *via* a variety of methods as detailed below. In this thesis, complexes of the "inorganic" fragment $MoXL_2(CO)_2$ are of major concern, and these were first prepared by Brisdon, Brown and Willis by the reaction of $Ph_4P[MoCl(bipy)(CO)_3]$ with 1,4-dichloro-2-butyne in 30:1 alcohol/water solutions[25-30]. A more systematic consideration of routes to η^3-butadienyl complexes is provided below. Recently a review[50] of both η^1- and η^3-butadienyl complexes has been published.

4.1 Methods of Preparation of Transition Metal η^3-Butadienyl Complexes

4.1.1 *Via* allenes

In addition to the iron complex discussed above, Green *et al* [3,4] have reported the preparation of a range of η^3-butadienyl complexes from the treatment of platinum or palladium phosphines with allenes of the form $H_2C=C=C(R)CH_2Cl$ (R=H, Me, Et) or with chloroprene, followed by silver or thallium hexafluorophosphate. The route to these cationic complexes is shown below (**Scheme 4.1.1**).

Scheme 4.1.1



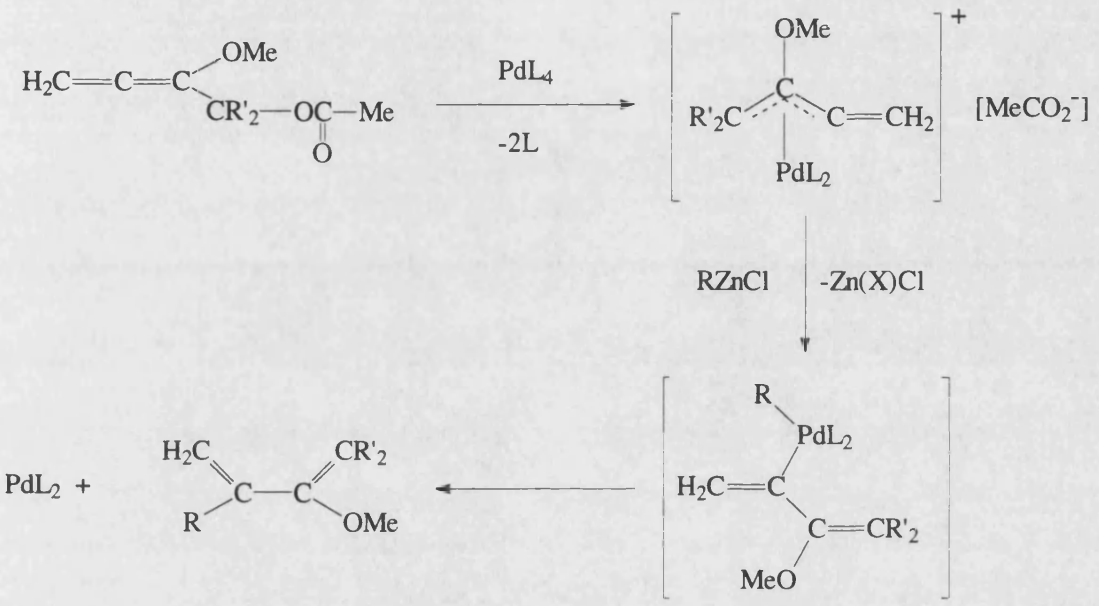
M=Pt; L_2=2PPh_3; R=H, Me, Et
M=Pt; L_2=dppf; R=H, Me, Et
[dppf=1,1-bis(diphenylphosphino)ferrocene]
M=Pd; L_2=2PPh_3; R=Et
(i)=[$Pt(C_2H_4)(PPh_3)_2$]
(ii)=[$Pt(C_2H_4)$(dppf)]
(iii)=[$Pd(PPh_3)_4$]

Typical reactions of these complexes will be discussed in **Section 4.3**.

Kleijn *et al*[5] have proposed a cationic palladium η^3-butadienyl complex as an intermediate in the process whereby the allenes H_2C=C=C(OMe)-CR'_2-X (R'=H, Me;

X=O_2CMe or O_2SMe) are converted to the 1,3-butadienes $H_2C{=}CR{-}C(OMe){=}CR'_2$ upon treatment with RZnCl in the presence of a catalytic quantity of $[Pd(PPh_3)_4]$. The proposed mechanism for one such complex is shown in **Scheme 4.1.2**.

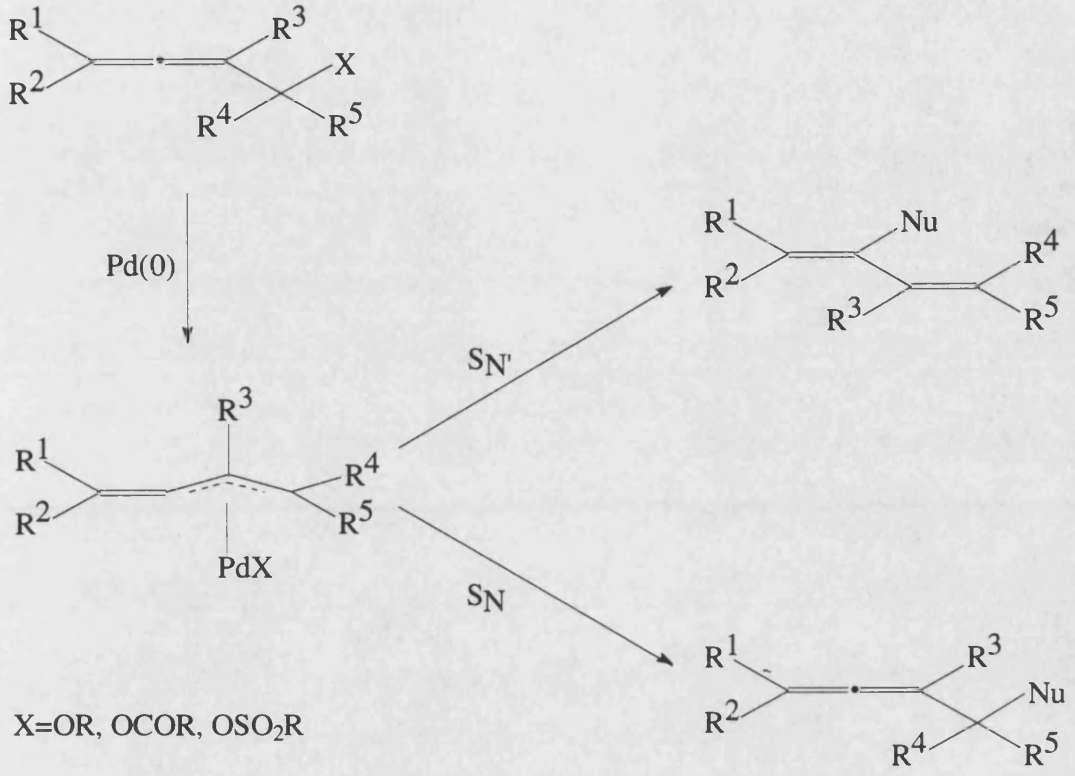
Scheme 4.1.2



L=PPh_3
R=$H_2C{=}CH{-}$; $Me_3SiC{\equiv}C{-}$; R'=H
R=$H_2C{=}CH{-}$; Ph ; *t*-$BuCH{=}CH{=}CH{-}$; $Me_3SiC{\equiv}C{-}$; $H_2C{=}C(Me){-}C{\equiv}C{-}$; R'=Me

A palladium η^3-butadienyl intermediate has also been proposed by Djahanbini *et al*[6] as an intermediate in the palladium(0) catalysed nucleophilic attack of sodium ethylmalonate upon α-allenic acetates or phosphates as shown in **Scheme 4.1.3**.

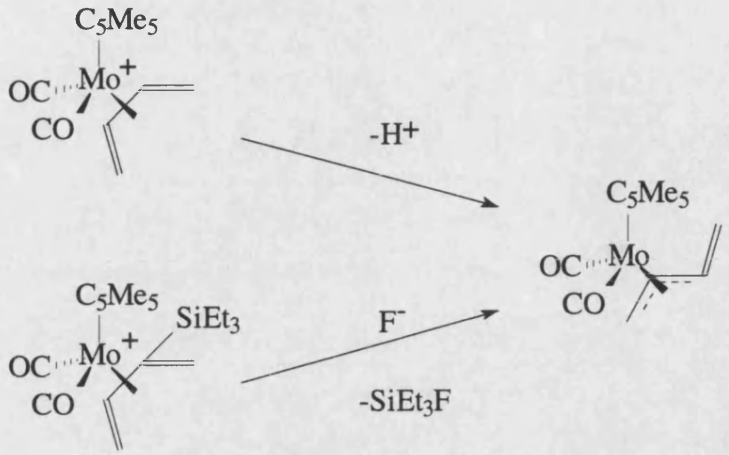
Scheme 4.1.3



4.1.2 *Via* deprotonation or desilylation of organic ligands

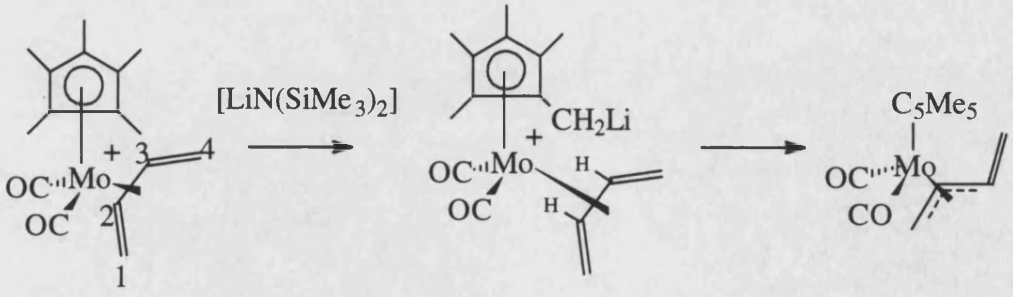
The cationic molybdenum η^4-diene complexes shown in **Scheme 4.1.4** have been reported[7,8] to undergo deprotonation and desilylation reactions respectively, leading to the formation of an η^3-butadienyl molybdenum complex.

Scheme 4.1.4



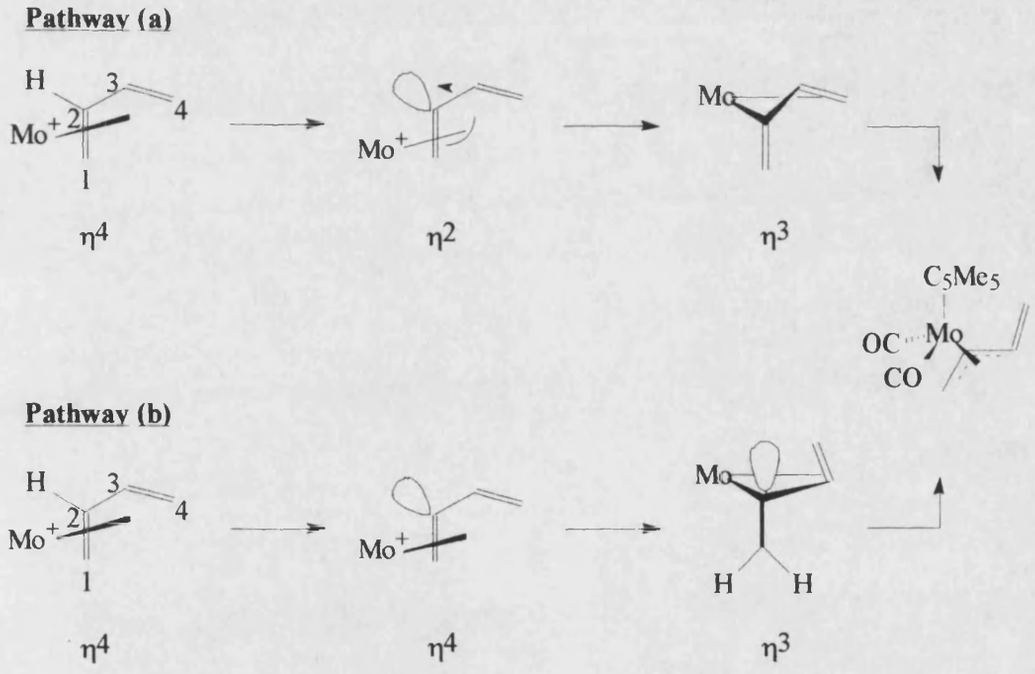
The deprotonation reaction fails if the η^5-C_5Me_5 ligand is replaced by either an η^5-indenyl or η^5-cyclopentadienyl ligand. This, together with the observed incorporation of deuterium into the methyl groups of the η^5-C_5Me_5 ligand upon treatment of the initial η^4-diene cation with triethylamine in $(CD_3)_2CO$, indicates that the reaction proceeds *via* an initial deprotonation of a methyl group (**Scheme 4.1.5**).

Scheme 4.1.5



An X-ray diffraction study of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2(\eta^3\text{-}CH_2CHC{=}CH_2)]$ showed that the η^3-allyl fragment of the butadienyl ligand adopts an *exo* orientation with respect to the C_5Me_5 ligand. This occurs because the 1,3-diene must adopt an *exo* orientation in order that the protons attached to **C2** or **C3** (as labelled below in **Scheme 4.1.6**) are in close proximity to the lithiated C_5Me_5 ligand. The butadienyl ligand exists in a transoid conformation however, whilst the initial 1,3-diene ligand has an s-*cis* conformation. Two possible pathways were proposed to account for this apparent rotation (**Scheme 4.1.6**).

Scheme 4.1.6



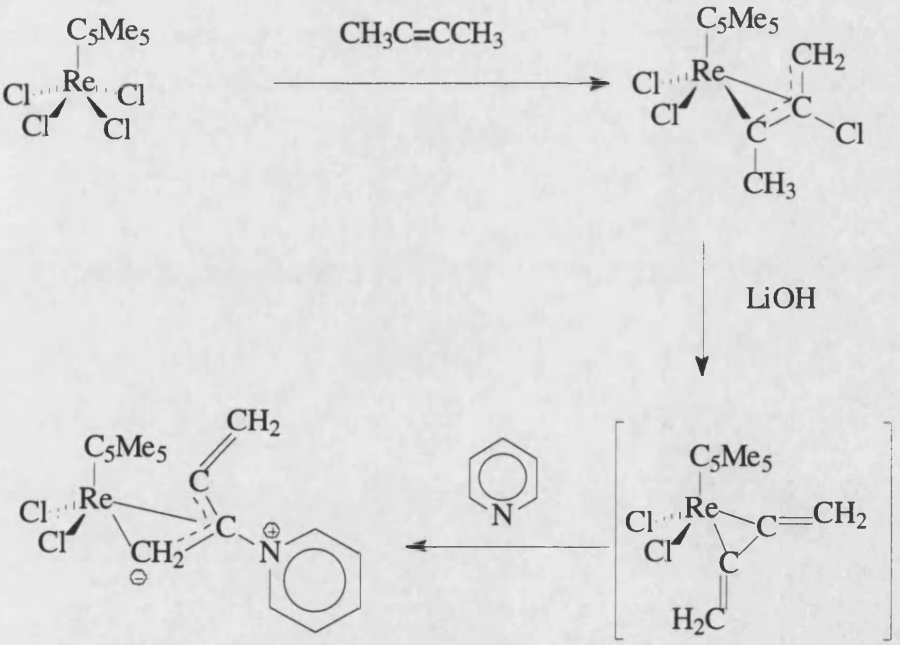
Pathway **(a)** occurs *via* initial deprotonation and a change in bonding mode from $\eta^4 \rightarrow \eta^2$, followed by rotation about the **C2-C3** axis; the **C2** lone pair can then interact with the metal centre. Pathway **(b)** involves a change from $\eta^4 \rightarrow \eta^3$ in the bonding

mode, and a net transfer of the metal centre positive charge to carbon. The actual pathway has yet to be determined.

Desilylation occurs by an analogous mechanism to that of the deprotonation reaction, with the action of the fluoride anion similar to that of the base. In addition the η^5-C_5H_5 analogues can be prepared.

Herrmann *et al* have reported[9] the preparation of an anionic rhenium η^3-butadienyl complex *via* the treatment of a rhenium(V) allylidene with a strong base in the presence of an excess of pyridine (**Scheme 4.1.7**).

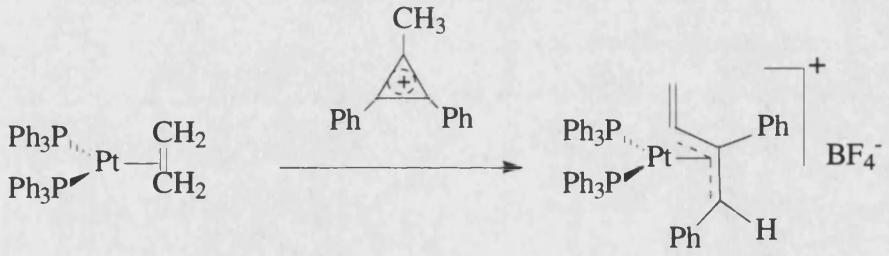
Scheme 4.1.7



4.1.3 *Via* ring-opening reactions

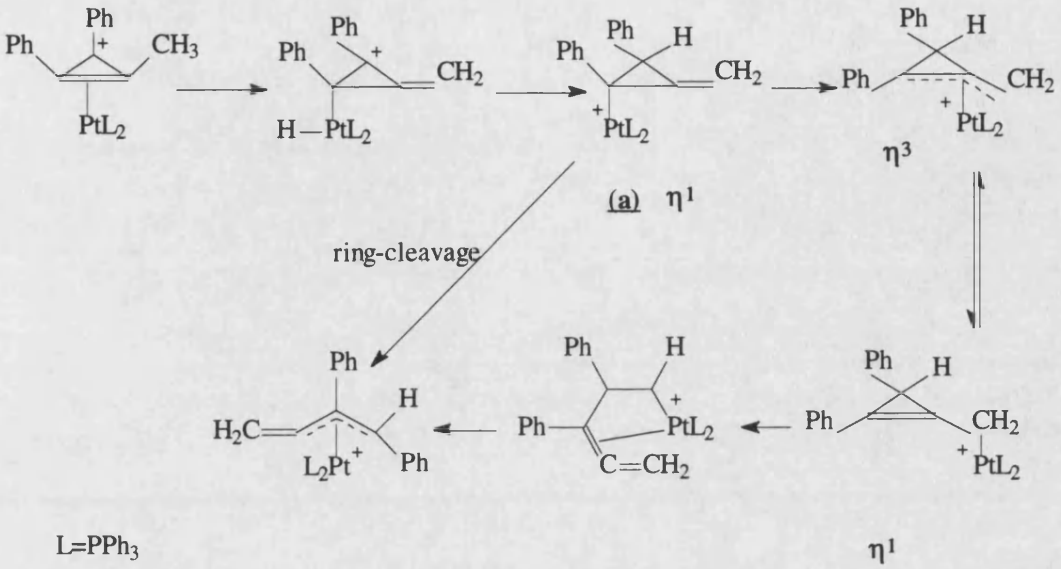
A novel ring-opening reaction of a cyclopropenyl ligand has been reported to lead to the formation of a cationic η^3-butadienyl platinum complex. The reaction of the triphenylcyclopropenyl cation with complexes containing the ML_2 fragment (M=Ni, Pd, Pt; L=PPh_3) had been shown previously[10,11] to give the expected η^2-complex, $[ML_2(\eta^2\text{-}Ph_3C_3)]^+$, however Hughes *et al*[12] found that the reaction of diphenylmethylcyclopropenyl cation with $[Pt(PPh_3)_2(C_2H_4)]$ gave the η^3-butadienyl complex following ring opening of the strained cyclopropenyl group, coupled with a hydrogen shift (**Scheme 4.1.8**).

Scheme 4.1.8



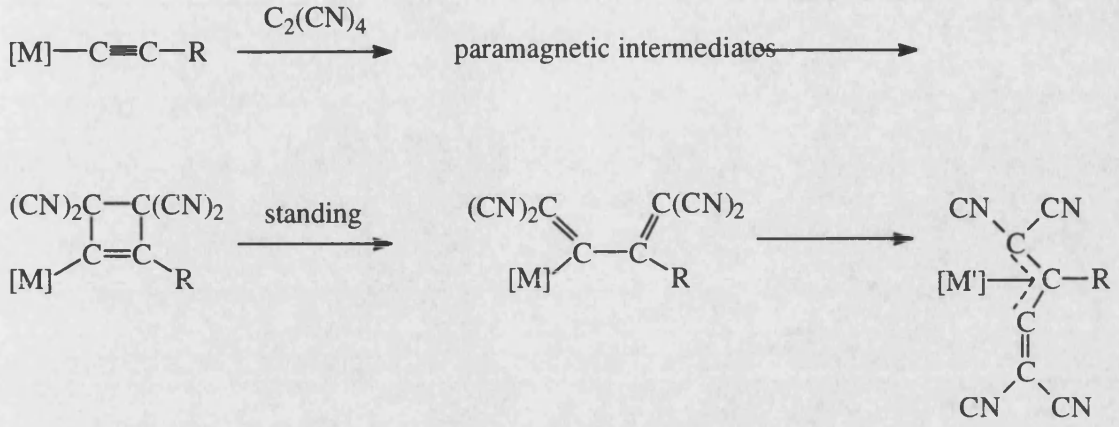
The mechanism of this reaction is as yet unknown, however two possibilities were proposed. One involves ring-opening of the coordinatively unsaturated intermediate (**a**), and the other $\eta^1 \rightarrow \eta^3 \rightarrow \eta^1$ isomerisation of (**a**), followed by subsequent ring-cleavage to yield the η^3-butadienyl complex (**Scheme 4.1.9**).

Scheme 4.1.9



Bruce and Snow and their co-workers have also produced a range of η^3-butadienyl complexes *via* ring-opening procedures[13-19]. In these cases ring-opening involves reacting a tungsten or ruthenium σ-acetylide complex, $L_nMC{\equiv}CR$, with tetracyanoethylene. The resulting σ-cyclobutenyl complex is slowly converted to a σ-butadienyl complex on standing which, on exposure to U.V. irradiation, rearranges to an η^3-butadienyl complex as shown in **Scheme 4.1.10**.

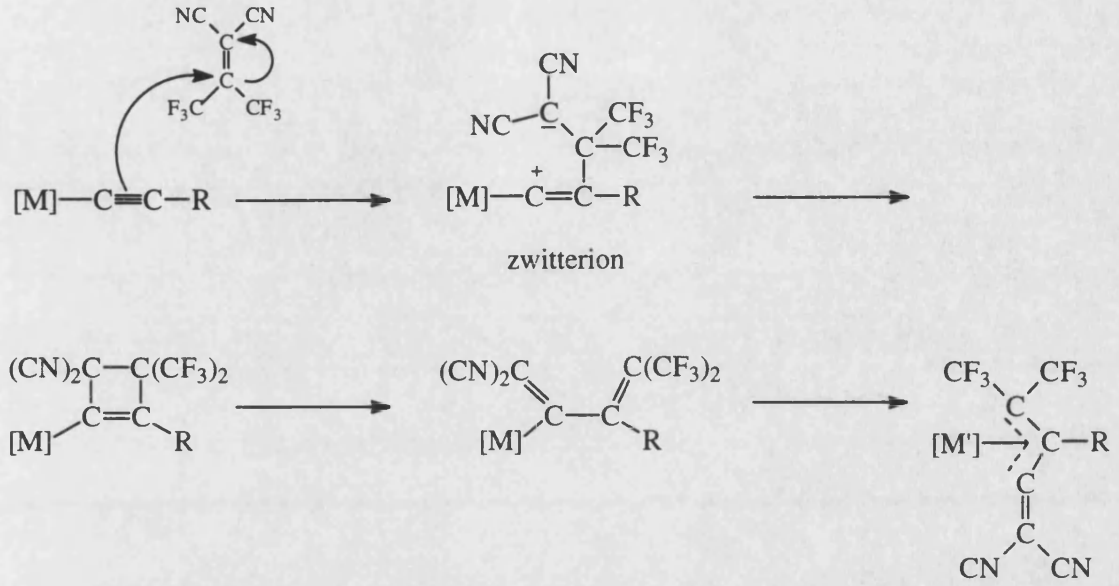
Scheme 4.1.10



R=Ph; [M]=$W(CO)_3(\eta^5\text{-}C_5H_5)$; [M']=$W(CO)_2(\eta^5\text{-}C_5H_5)$
R=Ph, Me; [M]=$Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)$; [M']=$Ru(PPh_3)(\eta^5\text{-}C_5H_5)$

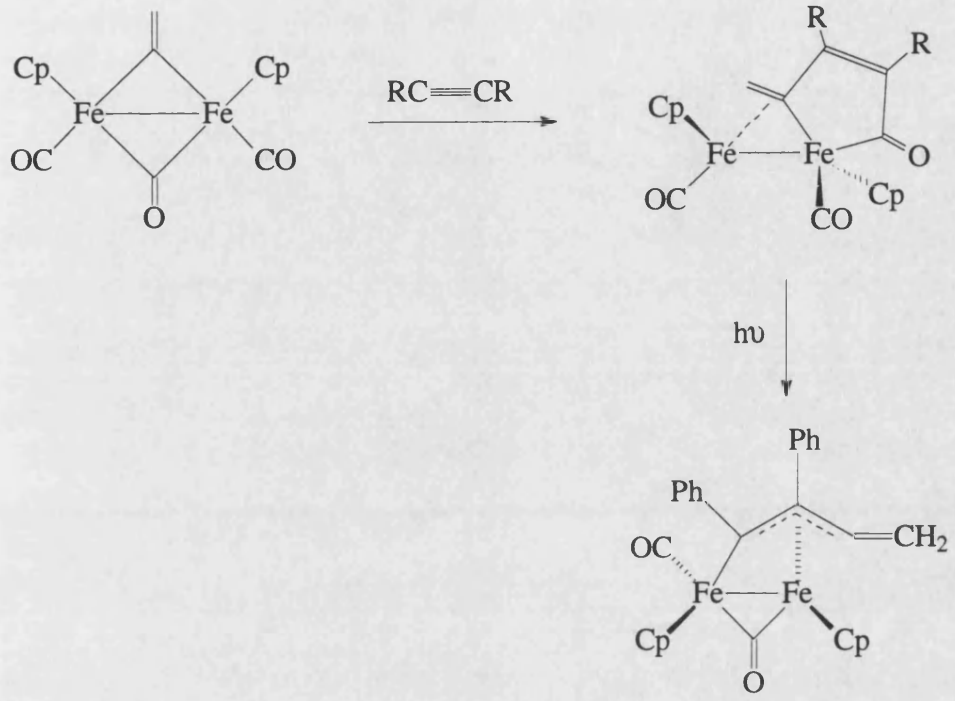
Similar compounds are also formed when 1,1-dicyano-2,2-bis(trifluoromethyl)ethene (dcfe) is employed in the first step[18]. In this case no paramagnetic intermediates were observed and the CF_3-bearing carbon of dcfe adds only to the β-carbon of the acetylide. Cyclisation then occurs selectively by bond formation between the α-carbon and the dicyanomethylene moiety, which can stabilise the negative charge in the intermediate zwitterion (**Scheme 4.1.11**).

Scheme 4.1.11



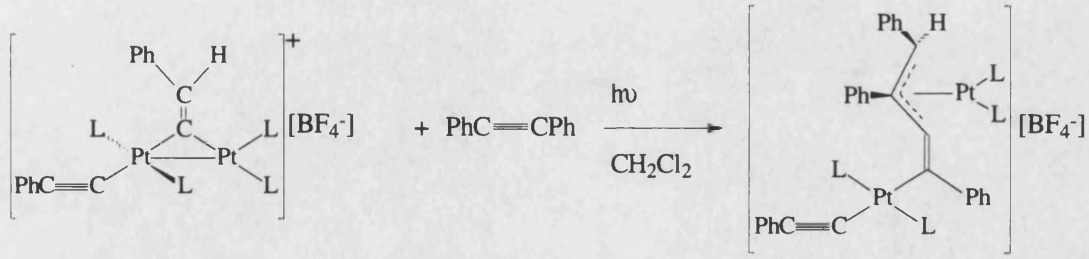
Casey *et al*[20] have reported that photolysis of the metallacyclopentenone $[CpFe(CO)]_2(\mu\text{-}\eta^2,\eta^2\text{-}COC(Ph)C(Ph)C{=}CH_2)]$ led to loss of CO and the formation of a butadienyl complex $[Cp_2Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Ph)C(Ph)C{=}CH_2\}]$ in which the allyl unit of the butadienyl ligand is bonded in a σ, π- fashion across the two iron atoms (**Scheme 4.1.12**).

Scheme 4.1.12



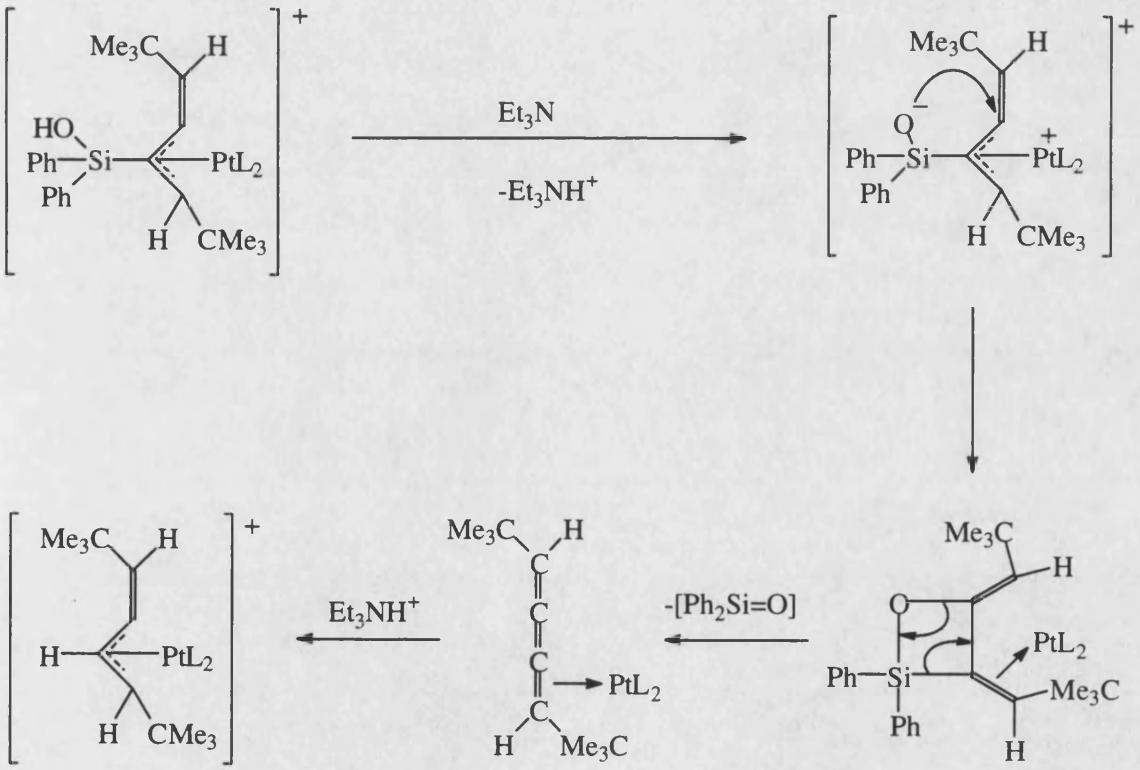
A similarly (μ-η^1,η^3) bonded butadienyl complex was prepared by Lukehart *et al*[21] *via* the reaction of a platinum μ-alkenylidene complex with diphenylacetylene as shown in **Scheme 4.1.13**, but no metal-metal linkage is present in this anion.

Scheme 4.1.13



The cationic η^3-butadienyl complexes $[Pt(PEt_3)_2\{\eta^3\text{-}C(H)(CMe_3)C(Si(OR)Ph_2)C{=}C(H)(CMe_3)\}][SbF_6]$ (R=H, alkyl) were prepared by Lukehart *et al*[22], from the reaction between *trans*-$[PtH(PEt_3)_2(THF)]^+$ and a dialkynylsilane in the presence of water or alcohol, which was believed initially to follow a mechanism involving a ring-opening process. However, a more recent paper[23] reported that the $SiPh_2(OR)$ substituent could be removed by triethylamine *via* an apparently unique base-promoted elimination. Protonation of an intermediate butatriene was initially believed to occur to give $[Pt(PEt_3)_2\{\eta^3\text{-}C(H)(CMe_3)C(H)C{=}C(H)(CMe_3)\}]^+$ *via* the following mechanism (**Scheme 4.1.14**).

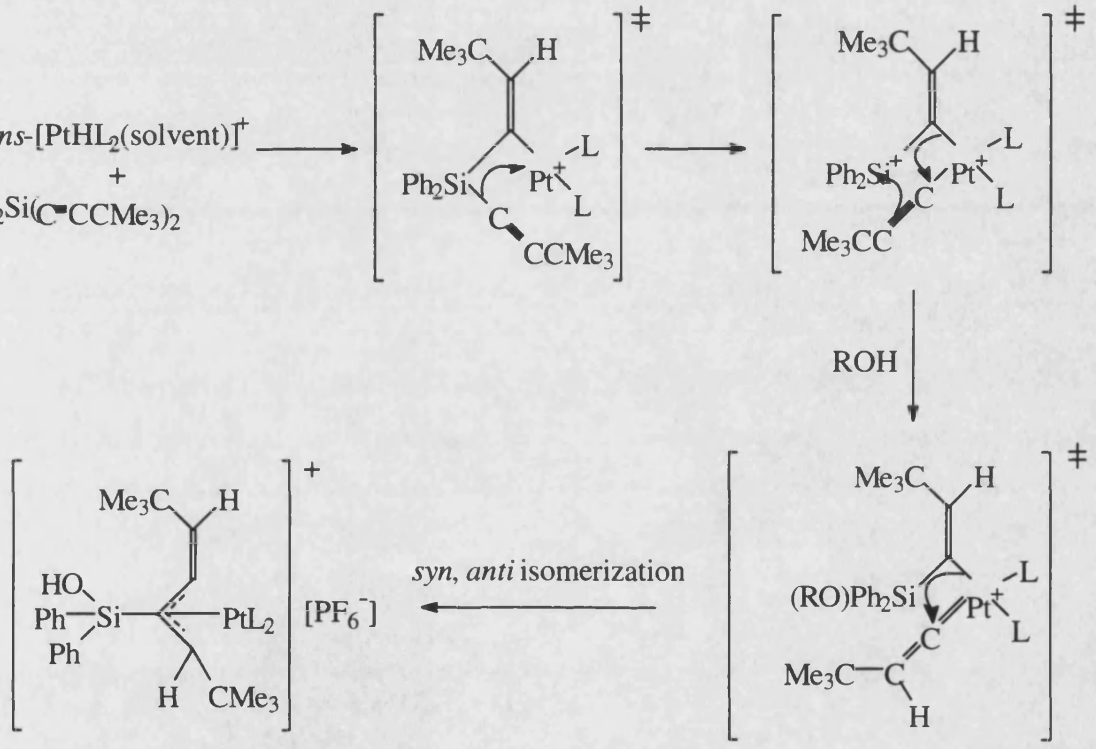
Scheme 4.1.14



L=PEt_3

A more detailed examination of the NMR data of this new non-(alkoxy)silyl-substituted complex led the authors to reassign the butadienyl protons of the original complex and consequently a revised mechanism, shown in **Scheme 4.1.15**, has now been proposed[23].

Scheme 4.1.15

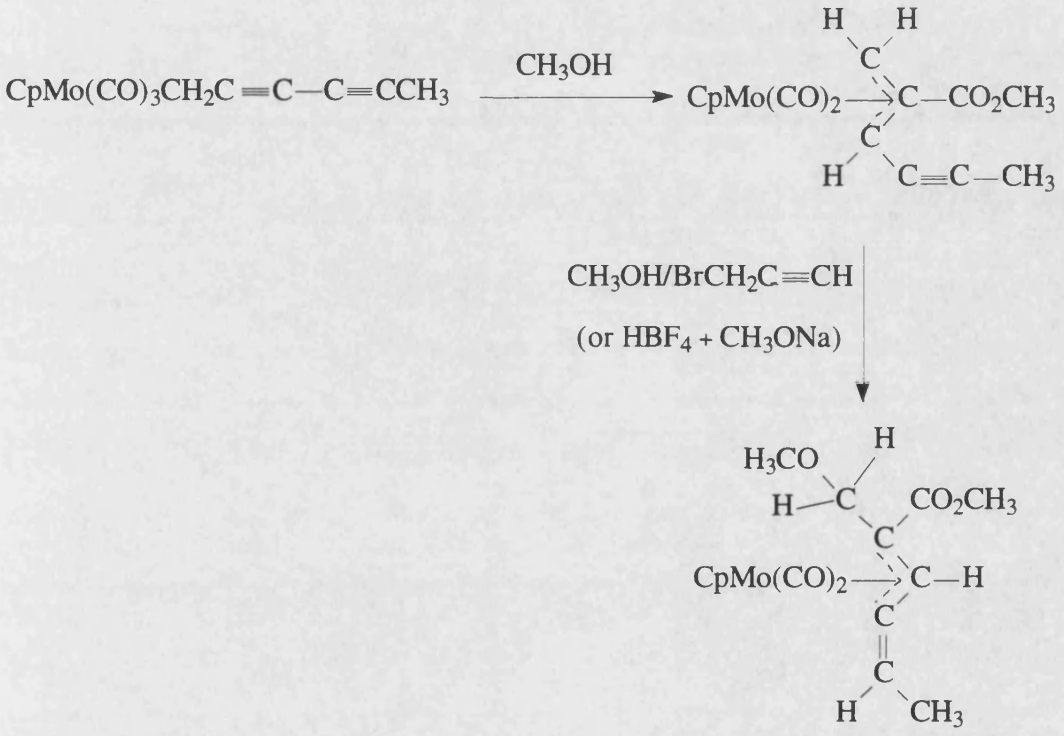


4.1.4 *Via* alkoxycarbonylation reactions

Giuliéri and Benaim have reported[24] the conversion of an η^1-diacetylinic complex of molybdenum to an η^3-butadienyl complex by the successive addition of two molecules of methanol as shown below (**Scheme 4.1.16**). The first addition, with insertion of a carbonyl ligand, gives the expected alkoxycarbonylated η^3-allyl complex. Subsequent 1,5-methanol addition to the unsaturated η^3-allyl ligand, a reaction which requires propargyl

bromide as catalyst, leads to an η^3-butadienyl complex. Protonation of an iron η^1-diacetylinic complex followed by reaction with methoxide ion gives the iron analogue of this complex. Further reaction of this with HBF_4 and sodium methoxide, with propargyl bromide as catalyst, leads to the η^3-butadienyl iron complex $[Fe(\eta^5\text{-}C_5H_5)(CO)\{\eta^3\text{-}CH_3OCH_2C(CO_2CH_3)CHC{=}CHCH_3\}]$.

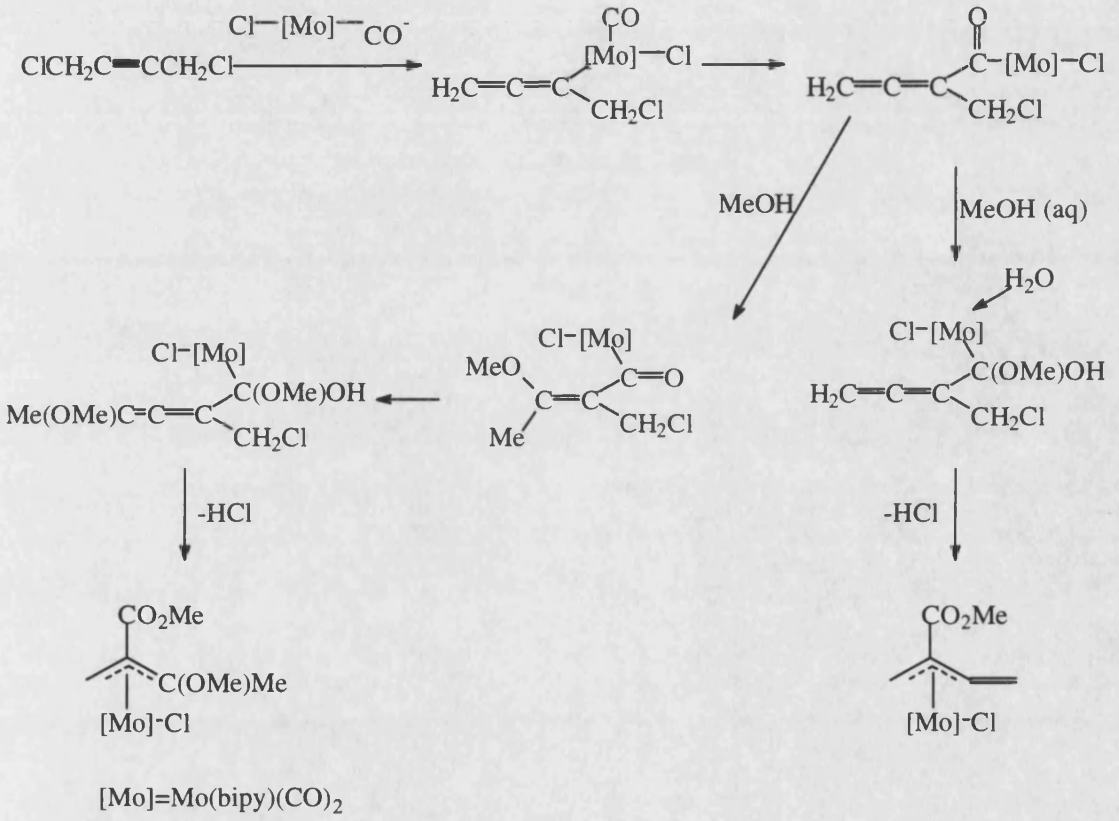
Scheme 4.1.16



Brisdon and his co-workers[25-30] have prepared a range of molybdenum η^3-butadienyl complexes *via* the reaction of 1,4-dichloro-2-butyne with the anion $[MoCl(bipy)(CO)_3]^-$ in wet alcohols. The complexes so produced are substituted at the central carbon of the allylic moiety by an ester group and are believed to be formed *via* an alkoxycarbonylation-type reaction. Under anhydrous conditions in THF/methanol[25,26],

the η^3-allyl complex [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CO_2Me)C(Me)(OMe)$}] is formed. **Scheme 4.1.17** shows a possible but unsubstantiated mechanism for the formation of these complexes.

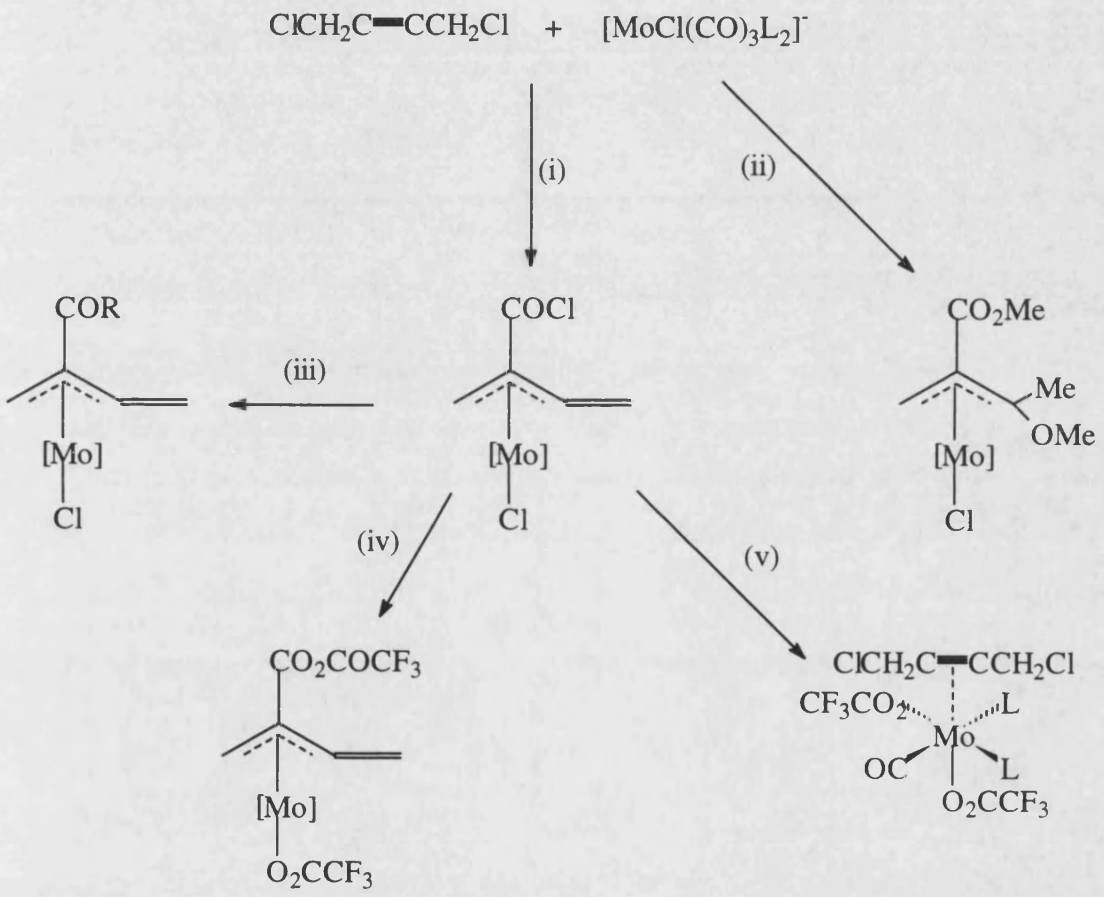
Scheme 4.1.17



The addition of excess primary or secondary aliphatic amines[27-29] to the initial reaction mixture gives rise to the corresponding amide-substituted complexes [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CONRR')C=CH_2$}] (R=H, R'=Me, Et, Pr^n, Ph, $CH_2CH=CH_2$, $CH_2C\equiv CH$; R=R'=Me, Et, Pr^n). The analogous acyl chloride- substituted complex[30], from which the above amide and ester complexes are available, can be isolated from the reaction between excess 1,4-dichloro-2-butyne and $[MoClL_2(CO)_3]^-$ as shown

in **Scheme 4.1.18**. This complex also reacts with $AgBF_4$ and excess $AgCO_2CF_3$ to give the carboxylate derivative containing an η^3-$CH_2C(CO_2COCF_3)C{=}CH_2$ ligand, whilst in the presence of excess 1,4-dichloro-2-butyne, this reaction gives the η^2-alkyne complex shown below.

Scheme 4.1.18



(i) $CHCl_3$, 20°C
(ii) MeOH/THF
(iii) MeOH or $HNEt_2$ or $H_2NCH(Me)Ph$
(iv) $AgBF_4/NaO_2CCF_3$/acetone, 20°C
(v) as (iv) with excess $ClCH_2C{\equiv}CCH_2Cl$

R=OMe, NEt_2, HNCH(Me)Ph
[Mo]=$[Mo(CO)_2L_2]$
L_2=bipy or phen

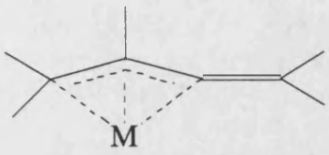
η^3-Butadienyl complexes of this type are the basis for much of the work reported later in this thesis and details of their structure, bonding and reactivity are given in the following sections.

4.2 Structure and Bonding in Transition Metal η^3-Butadienyl Complexes

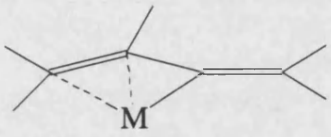
Table 4.2.1 overleaf lists the relevant bond lengths and angles for those complexes whose structures have been determined by X-ray crystallography. In general the data reported show, as expected, that the η^3-butadienyl ligand is bound to the metal in a similar fashion as is an η^3-allyl moiety, but with a terminal, uncoordinated $C=CR_2$ substitution. An apparently anomalous uncoordinated C=C double bond length of *ca*1.45Å (*cf* 1.26-1.38Å for the other η^3-butadienyl complexes and 1.344±0.001Å in free butadiene[31]) was reported[25] for the complex $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CO_2Me)C=CH_2\}]$ and was rationalised as resulting from interactions analogous to those found in η^4-butadiene complexes in which anti-bonding diene orbitals are populated[32,33].

Many of the η^3-butadienyl complexes whose structures have been reported exhibit a short M-C(2) bond length (see overleaf for numbering scheme), consistent with some degree of localised bonding. This, together with the asymmetry apparent within the η^3-allyl moiety indicates that structures (**A**) and (**B**) (as labelled in **Figure 4.2.1** below) may be considered as bonding extremes for the η^3-butadienyl ligand. A contribution from the allene-type structure (**C**) is also evident in many instances from an examination of the C-C bond distances. The complexes prepared by Bruce *et al*[13-19] contain electron-withdrawing cyano and trifluoromethyl substituents and the short M-C(2) bond lengths together with the appearance of the quaternary carbon at surprisingly low fields in the ^{13}C NMR spectrum (δ210-240ppm) suggest that structure (**D**) may make a major contribution to the bonding in some complexes.

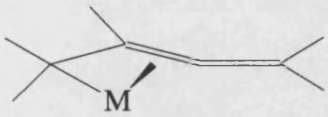
Figure 4.2.1:-*Bonding extremes found in η^3-butadienyl complexes*



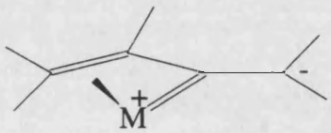
(A)



(B)



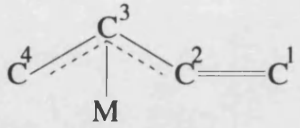
(C)



(D)

Further comparisons between the bonding and reactivities of the complexes $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2(\eta^3\text{-}CH_2CHC{=}CH_2)]$ and $[MoXL_2(CO)_2\{\eta^3\text{-}CH_2C(CONRR')C{=}CH_2\}]$ in particular are contained in **Section 4.3**.

Table 4.2.1



Complex	C(1)-C(2) Å	C(2)-C(3) Å	C(3)-C(4) Å	M-C(2) Å	M-C(3) Å	M-C(4) Å	C(1)-C(2)-C(3) (°)	C(2)-C(3)-C(4) (°)	Ref
[CpFe(PPh$_3$){η^3-$CF_2C(CF_3)C{=}C(CF_3)_2$}]	1.319(8)	1.442(8)	1.426(9)	1.905(6)	1.981(7)	1.969(7)	134.5(7)	—	1, 2
[Pt(PPh$_3$)$_2${η^3-$CH_2C(Et)C{=}CH_2$}][PF_6]	1.26(4)	1.44(3)	1.42(3)	2.09(2)	2.20(2)	2.20(2)	141(2)	117(2)	3, 4
[(η^5-C_5Me_5)Mo(CO)$_2$(η^3-$CH_2CHC{=}CH_2$)]	1.353(24)	1.391(20)	1.348(22)	2.198(15)	2.208(14)	2.328(13)	139(1)	120(1)	7,8
[(η^5-C_5Me_5)$ReCl_2${η^3-$H_2CC(C_5H_5N)CCH_2$}]	1.337(9)	1.428(8)	1.445(9)	2.046(7)	2.111(6)	2.190(6)	134.1(7)	113.0(6)	9
[Pt(PPh$_3$)$_2${η^3-$CH(Ph)C(Ph)C{=}CH_2$}][BF_4]	1.31(2)	1.46(2)	1.40(2)	2.075(13)	2.201(14)	2.291(14)	140(1)	115(1)	12
[CpRu(PPh$_3$){η^3-$C(CN)_2C(Ph)C{=}C(CN)_2$}]	1.383(6)	1.432(7)	1.476(6)	1.919(5)	2.135(4)	2.231(4)	—	—	13

Table 4.2.1 (cont.)

Complex	C(1)-C(2) Å	C(2)-C(3) Å	C(3)-C(4) Å	M-C(2) Å	M-C(3) Å	M-C(4) Å	C(1)-C(2)-C(3) (°)	C(2)-C(3)-C(4) (°)	Ref
[CpRu(Ph_3P){η^3-$C(CF_3)_2C(Ph)C=C(CN)_2$}]	1.37(1)	1.42(1)	1.46(1)	1.977(7)	2.138(7)	2.202(7)	131.4(7)	113.5(6)	18
[CpRu(CO){η^3-$CH(CO_2Me)C(Ph)C=C(CN)(CO_2Me$}]	1.344(5)	1.422(5)	1.431(5)	2.047(4)	2.160(4)	2.218(4)	136.5(4)	114.2(3)	19
[$Pt(PEt_3)_2$){μ-η^1, η^3-C(Ph)(H)C(Ph)C=C(Ph)} $Pt(PEt_3)_2(C\equiv CPh)$][BF_4]	1.29(1)	1.38(1)	1.43(1)	2.17(1)	2.23(1)	2.18(1)	146(1)	114(1)	21
[$Pt(PEt_3)_2$){η^3-$CH(CMe_3)C(SiPh_2OH)C=CHCMe_3$)}]	2.11(1)	1.43(1)	1.42(1)	2.11(1)	2.19(1)	2.27(1)	150(1)	117(1)	22
[MoCl(bipy)$(CO)_2$){η^3-$CH_2C(CO_2Me)C=CH_2$}]	1.45(5)	1.41(5)	1.44(5)	2.22(3)	2.22(3)	2.32(4)	148.3(35)	116.2(10)	25
[Mo($O_2CC_3F_7$)(bipy)$(CO)_2$){η^3-$CH_2C(CONHMe)C=CH_2$}]	1.335(18)	1.399(18)	1.416(17)	2.200(10)	2.235(10)	2.314(10)	141.7(13)	112.5(10)	27,29

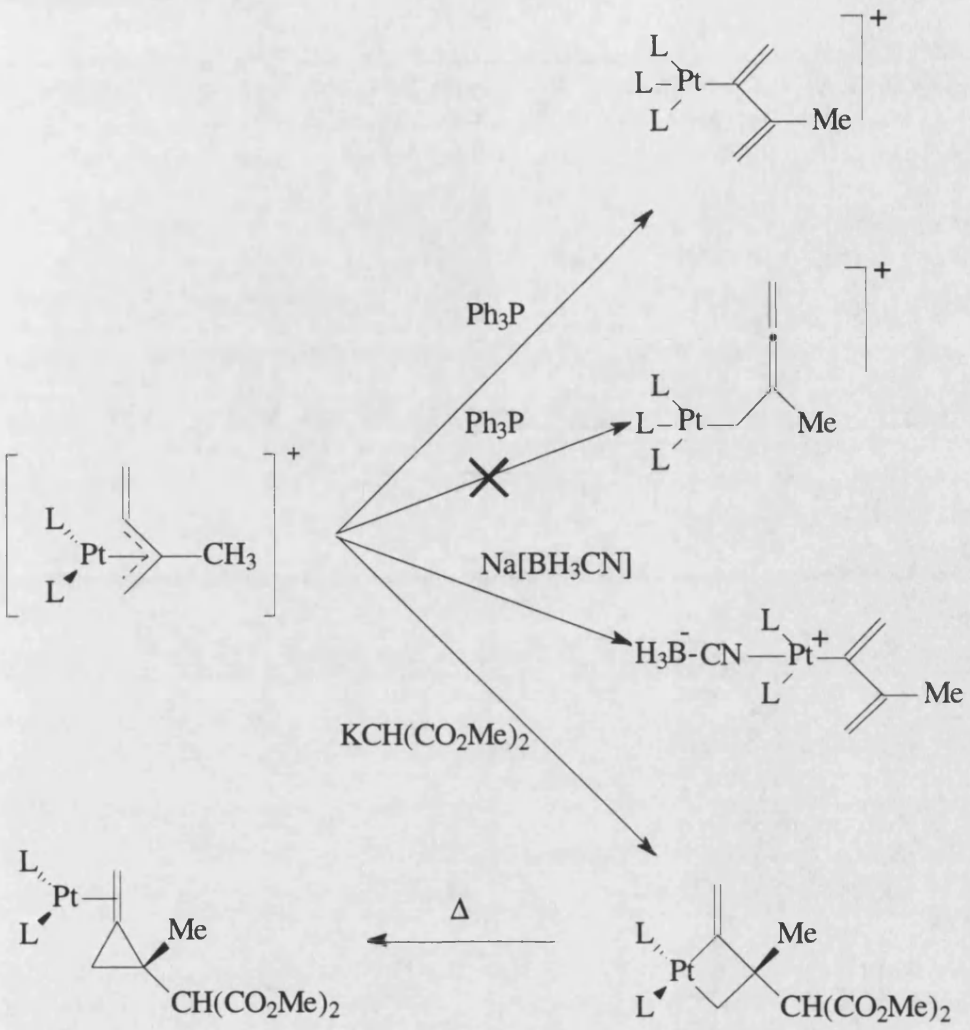
4.3 Reactivity of Transition Metal η^3-Butadienyl Complexes

To date the reactivities of transition metal η^3-butadienyl complexes in general, and those of the early transition metals in particular have been relatively unexplored, particularly compared to the large amount of work published on the η^3-allyl complexes. The area is one of great potential interest as reactions could occur both upon the η^3-allyl moiety (thus providing comparisons with η^3-allyl complexes) and also upon the uncoordinated C=C double bond moiety. The few published examples of reactivity studies and reactions upon η^3-butadienyl complexes are outlined below.

4.3.1 Reactivity of $[Pt(PPh_3)_2\{\eta^3\text{-}CH_2C(R)C{=}CH_2\}][PF_6]$

The preparation of these cationic η^3-butadienyl complexes was discussed earlier in **Section 4.1.1**. A preliminary reactivity study[3] was carried out on a complex (R=Me) involving reactions with several nucleophiles toward which it is highly reactive (**Scheme 4.3.1**).

Scheme 4.3.1



L=PPh_3

The reaction of triphenylphosphine with $[Pt(PPh_3)_2(\eta^3\text{-}CH_2C(Me)C{=}CH_2)]^+$ gave the cationic 1,3-diene complex $[Pt(PPh_3)_3\{\eta^1\text{-}C(=CH_2)\text{-}C(Me){=}CH_2\}]^+$ following attack at the platinum centre, and a change in the bonding mode of the butadienyl ligand from η^3 to η^1. The isomeric complex, a 1,2- rather than a 1,3-diene, was not observed.

The complex $[(H_3B\text{-}CN)Pt(PPh_3)_2\{\eta^1\text{-}C(=CH_2)\text{-}C(Me)=CH_2\}]$ was obtained from the reaction with $Na[BH_3CN]$, the anion attacking the metal centre rather than the organic fragment and acting as an N-bonded ligand.

Attack by the soft carbon nucleophile $[CH(CO_2Me)_2]^-$ would be expected to occur at either **C**^{1} or **C**^{4} of the η^3-butadienyl ligand, giving a Pt(0) allene or vinylcarbene complex respectively. However in this instance nucleophilic attack occurred selectively at the central carbon of the allylic moiety, **C**^{2}, to produce an *exo*-2-methyleneplatinacyclobutane (which was converted by thermolysis to a Pt(0) methylenecyclopropane complex). This selectivity is surprising as attack at the terminal carbons of $[M(PPh_3)_2(\eta^3\text{-allyl})]^+$ (M=Pd, Pt) has been extensively documented[34,35] whereas nucleophilic attack at the central carbon of an η^3-allylic ligand is still uncommon.

4.3.2 Reactivity of $[Mo(\eta^5\text{-}C_5Me_5)(CO)_2(\eta^3\text{-}CH_2CHC=CH_2)]$

This complex was obtained[7,8] by reaction of a cationic η^4-diene molybdenum complex with the base $Li[N(SiMe_3)_2]$ at low temperature as shown in **Scheme 4.1.4**. In order to explore the possibility of reversing the reaction, *ie.* protonating this complex to regenerate the original η^4-diene complex, an extended Hückel molecular orbital calculation study was performed to assess the susceptibility of the complex towards electrophilic attack[8]. Charge-controlled electrophilic attack would be expected to occur at the site possessing the largest negative charge whilst frontier-orbital controlled electrophilic attack would take place at the site with the largest MO coefficient in the HOMO.

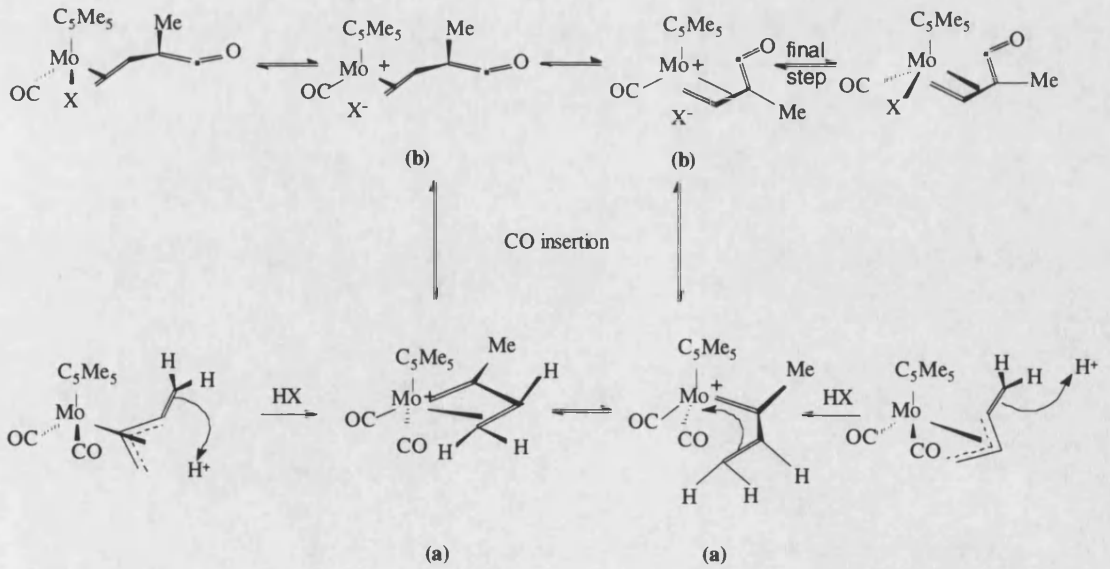
The EHMO calculations predicted attack would occur at the terminal methylene carbon whether the reaction was charge- or frontier-orbital controlled, this site having the

largest negative charge of -0.35e and also the only significant HOMO coefficients. Thus the reaction should not be reversible as attack at this position by H^+ would yield an η^3-vinylcarbene type of complex.

In order to test this prediction experimentally, the η^3-butadienyl complex was treated with trifluoromethanesulphonic acid at low temperature. The product could not be identified but upon treatment with lithium iodide it yielded an η^4-vinylketene complex, $[Mo(\eta^5\text{-}C_5Me_5)I(CO)\{\eta^4\text{-}CH_2{=}CHC(CMe){=}C{=}O\}]$, the structure of which was determined by X-ray crystallography.

This reaction is believed to proceed *via* the expected η^3-vinylcarbene (**a**), formed by protonation of the η^3-butadienyl ligand, followed by carbonyl insertion into the metal-carbon double bond, and subsequent capture of the 16-electron species (**b**) by the triflate anion (**Scheme 4.3.2**).

Scheme 4.3.2



The η^4-vinylketene complex is converted quantitatively to the original η^3-butadienyl complex by treatment with triethylamine, which appears to indicate that the final step (marked thus above) is reversible, the complex being regenerated by proton abstraction from complex (**a**).

4.3.3 Reactivity of $[Mo(O_2C_3F_7)(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2\}]$

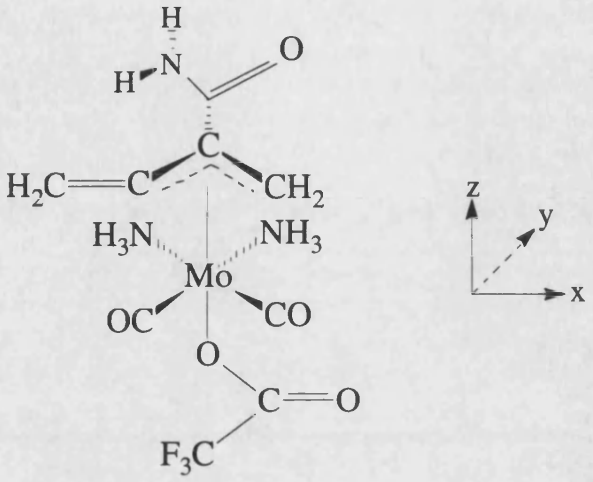
In order to conform to the noble gas formalism or 18-electron rule, η^3-butadienyl complexes are considered to be η^3-bonded to metal d^4 complexes. An isolobal treatment shows that for a suitable bonding interaction the butadienyl fragment binds as a double bond substituted η^3-C_3H_5 moiety, rather than as a neutral or negatively charged η^4-C_4H_6 moiety.

A theoretical study based on the $[Mo(O_2C_3F_7)(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2\}]$ system has been carried out[29] to determine the degree to which the double bond is conjugated with the allyl π-system, and to determine the probable centres of reactivity of the butadienyl ligand in this complex.

Several simplifications and assumptions were made to the system. The complex was assumed to be of regular octahedral geometry with the plane of the allyl system perpendicular to the z-axis of the complex and its centroid directly above the molybdenum atom. Also, several of the ligands were simplified to reduce the number of atoms involved in the calculations. The following model structure (**Figure 4.3.1**) was thus treated by an extended Hückel molecular orbital approach.

Figure 4.3.1:- ***Model complex***

[Mo(O$_2$CCF$_3$)(NH$_3$)$_2$(CO)$_2${η^3-CH$_2$C(CONH$_2$)C=CH$_2$}]

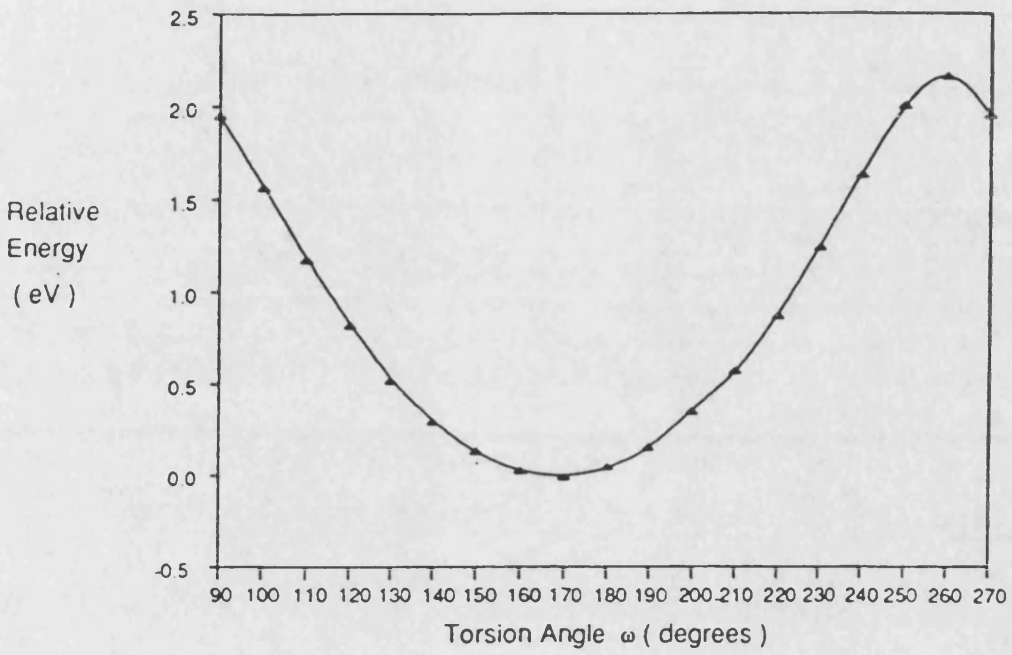


The 2,2'-bipyridyl and the $O_2C_3F_7$ ligands were modelled as two ammonia molecules and an O_2CCF_3 group respectively, and the amide methyl group treated as a proton. Idealised C-H and N-H bond lengths were used with the other interatomic distances and angles being taken from the X-ray structure of the complex.

The calculations indicated that:-

(i) the minimum energy for the π-system is at an angle (ω) of 170° where the π-allyl and the C=CH$_2$ units are unconjugated. The unconjugated form is favoured by approximately 2.2eV (**Figure 4.3.2**).

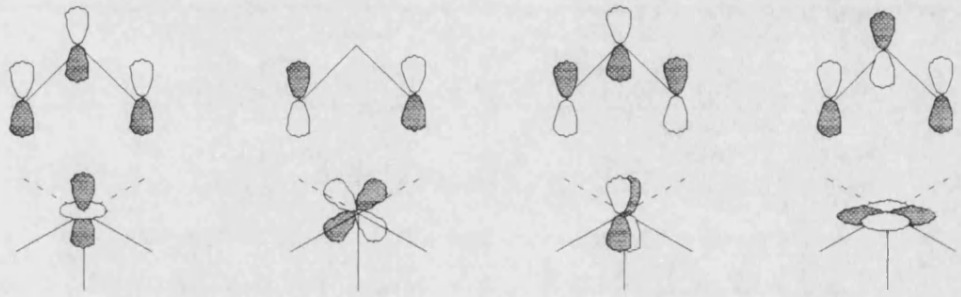
Figure 4.3.2


Relative
Energy
(eV)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270
Torsion Angle ω (degrees)

(ii) the π and π^* orbitals of the terminal C=C double bond remain largely unchanged in energy on complexation and hence the double bond can be expected to react independently of the allyl system.

The interactions between the metal d-orbitals and the allyl orbitals are shown below (**Figure 4.3.3**) (*n.b.* the metal d_{xy} orbital does not appear to be significantly involved in bonding to the allyl π-system).

Figure 4.3.3



A **B** **C**

A:- d_z2-Ψ_1 (bonding) **B**:- d_{xy}-Ψ_2 (nonbonding) **C**:- d_{yz}, $d_x2_{-y}2$-Ψ_3 (antibonding)

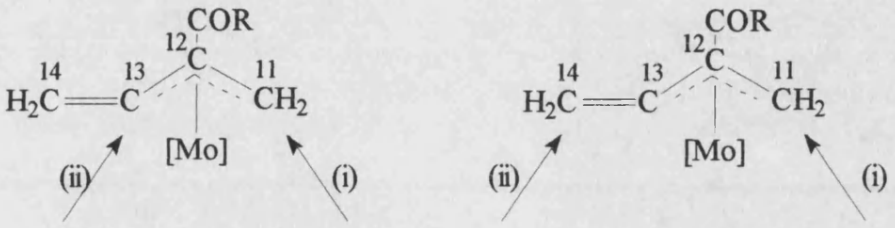
(iii) the carbon atom with the most positive net charge was found to be $\mathbf{C_{13}}$ and charge-controlled nucleophilic attack can be expected to occur here. If the reaction is frontier molecular orbital controlled, nucleophilic attack would occur preferentially at $\mathbf{C_{11}}$, which is less sterically hindered.

Electrophilic attack, if charge-controlled, is predicted to occur at $\mathbf{C_{14}}$ which has the most negative net charge, whereas frontier molecular orbital controlled attack will occur at $\mathbf{C_{11}}$, the carbon atom with the largest coefficient in the HOMO, which is

composed of a combination of the d_{yz} and ψ_3^* orbitals. These predictions are summarised below in **Scheme 4.3.3**.

Scheme 4.3.3

Nucleophilic attack **Electrophilic attack**



(i):- FMO contolled attack
(ii):- Charge-controlled attack

Further investigations into the reactivity of these complexes was carried out as part of the research programme reported in this thesis and the results are discussed in the following section.

4.4 DISCUSSION

In order to test experimentally the theoretical predictions outlined previously, a representative range of complexes containing the η^3-butadienyl ligand were prepared and subsequently reacted with a variety of reagents ranging from neutral (Br_2) and charged (H^+) electrophiles to neutral (triphenylphosphine) and charged (dimethylmalonate anion) nucleophiles. Thus it was hoped that a general picture of the reactivity of molybdenum η^3-butadienyl complexes could be built up to test the validity of the theoretical study.

The route to the η^3-butadienyl complexes **(16)**, **(17)** and **(18)** involves a three step sequence, the first two reactions afford a virtually quantitative yield (**Scheme 4.4.1**).

Scheme 4.4.1

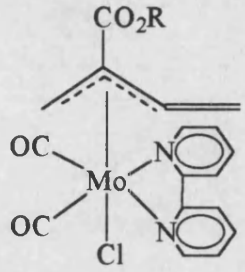
$[Mo(CO)_6]$ + 2,2'-bipyridyl ⟶ $[Mo(bipy)(CO)_4]$

Complex (14)

$[Mo(bipy)(CO)_4]$ + Ph_4PCl ⟶ $Ph_4P[MoCl(bipy)(CO)_3]$

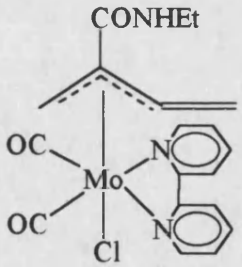
Complex (15)

$Ph_4P[MoCl(bipy)(CO)_3]$ + $ClCH_2C{=}CCH_2Cl$ + ROH ⟶



Complex (16) (R=Me)
Complex (17) (R=Et)

$Ph_4P[MoCl(bipy)(CO)_3]$ + $ClCH_2C{=}CCH_2Cl$ + $EtNH_2$ ⟶



Complex (18)

Complexes (**14**)[36], (**15**)[37], (**16**)[25], (**17**)[26, 28] and (**18**)[27, 29] were prepared in 98%, 95%, 49%, 38%, and 52% yield respectively, according to literature procedures, or minor variations thereof.

4.4.1 Reactions on [MoCl(bipy)(CO)$_2${η^3-$CH_2C(COR)C=CH_2$}] (R=OMe (16), OEt(17), NHEt(18))

4.4.1.1 Bromination

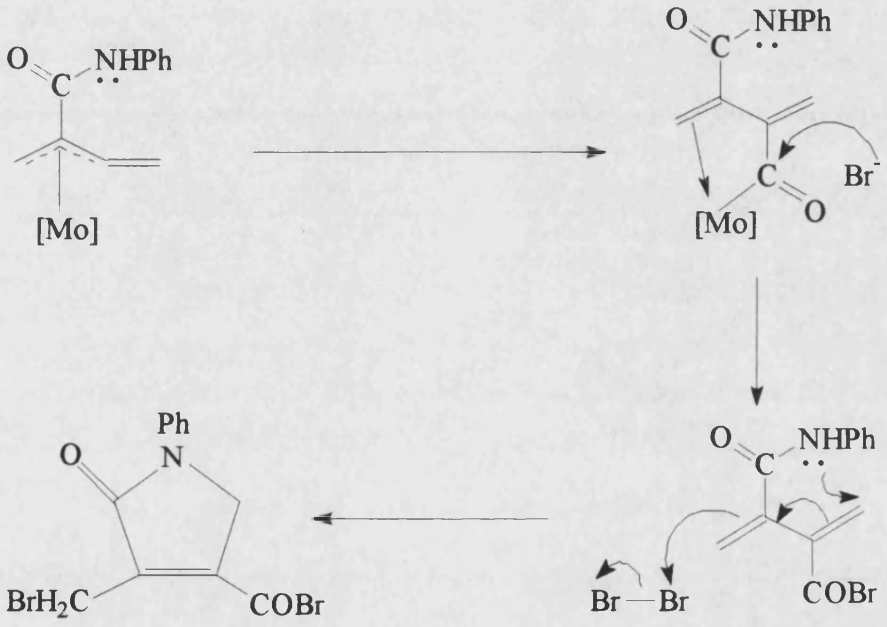
In a final year Bath project report[38], it was previously reported that the bromination of [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CO_2Me)C=CH_2$}] (**16**) in dichloromethane at -78°C led after column chromatography of the products to the isolation of CH_2=CBr-$C(CO_2Me)$=CH_2. However the proton NMR spectrum of the organic product exhibited three singlet peaks at δ4.84, 4.42 and 3.88ppm with relative intensities of 2:2:3 respectively, whereas the NMR spectrum of the proposed monobrominated butadiene would be expected to show coupling between the vinylic protons with J~2Hz.

Thus, the bromination of complex (**16**) was repeated using 2.1 equivalents of molecular bromine in order to completely brominate the metal fragment as well. A yellow oil (**19**) with identical NMR data to those previously reported was isolated in moderate yield. The mass spectrum of (**19**) has M^+=351, and from the 1:3:3:1 intensity pattern of the molecular ion it is apparent that (**19**) is a tribrominated and not a monobrominated species. The ester group is still intact, with the infra-red spectrum of (**19**) showing a carbonyl absorption at 1720cm^{-1}.

The ^{13}C NMR spectrum of (**19**) shows the carbonyl carbon resonance at δ163.4 with olefinic carbons at δ141.1 and 132.2, two methylene signals at δ53.1 and 34.5, and the ester methyl group resonating at δ31.6. From these data (**19**) was formulated as $BrCH_2$-$C(CO_2Me)$=C(Br)-CH_2Br. The bromination of complex (**17**) gave analogous results with $BrCH_2C(CO_2Et)$=C(Br)-CH_2Br (**20**) being isolated as a yellow oil. Satisfactory elemental analyses for both compounds were obtained.

Bromination of [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CONHPh)C=CH_2$}] was also attempted as part of a final year project[39], and the organic product finally isolated was formulated as a dibrominated species with the molecular formula $C_{12}H_9Br_2NO_2$. Based on spectroscopic data, the product was designated as a pyrrolidine system, possibly formed *via* the mechanism shown below (**Scheme 4.4.2**).

Scheme 4.4.2

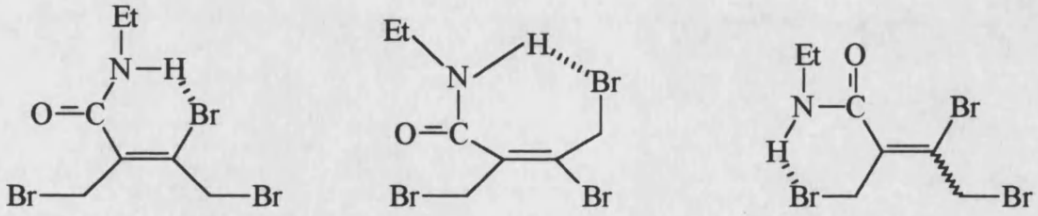


The bromination of [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CONHEt)C=CH_2$}] (**18**) was undertaken, again using 2.1 equivalents of molecular bromine, and a white solid (**21**) was isolated by column chromatography. The infra-red spectrum of (**21**) showed an N-H peak at 3260cm^{-1}, with no peak corresponding to the acyl bromide in the above pyrrolidenone system. The mass spectrum indicated that the structure of (**21**) is again that of a tribrominated species, with M^+=364. From the elemental analysis (**21**) is formulated as $C_7H_{10}Br_3NO$, which indicates that an analogous product to the tribrominated esters (**19**)

and (**20**) has been formed, *i.e.* $BrCH_2$-C(CONHEt)=C(Br)-CH_2Br. The proton NMR spectrum of (**21**) showed a broad singlet at δ6.15 corresponding to the -CONHEt proton. The ethyl group appears as a three proton singlet centred at δ1.26, with the methylene protons at δ3.44, split into two quartets by the amide proton. One of the two methylene bromide groups resonates as a two proton singlet at δ4.28 whilst the other is split into two singlets at δ4.42 and 4.31 with relative intensities of about 9:1 respectively.

These observations are consistent with the existence in solution at ambient temperature of more than one stable conformer. Both *cis* and *trans*-isomers may be stabilised by hydrogen bonding between the amide proton and a bromine atom. Hydrogen bonding in the *cis*-isomer **(i)** (shown below in **Scheme 4.4.3**) would produce a stable, planar, six-membered ring system, compared with a seven-membered non-planar ring system formed in the *trans*-isomer **(ii)**. Either isomer could also show conformation **(iii)**, which contains a six-membered, hydrogen-bonded ring system.

Scheme 4.4.3



(i) **(ii)** **(iii)**

Further evidence in support of H-bonding in (**21**) comes from the infra-red spectrum in which the amide carbonyl band appears at $1540cm^{-1}$, a value typical for hydrogen bonded amides where the carbonyl group is shifted to a lower frequency. The

^{13}C NMR spectrum of (**21**) was not informative as it showed no clear carbonyl or alkene resonances. A methyl signal was found at δ14.53 and five CH_2 resonances at δ35.68, 35.09, 33.02, 31.75 and 28.54 ppm again indicating the co-existence of more than one isomer. Recrystallisation of (**21**) afforded fine white needles, which could not be obtained in a suitable form for X-ray crystallography.

4.4.1.2 Reaction of methanesulphonic acid with [MoCl(bipy)(CO)$_2${η^3-CH$_2$C(CO$_2$Et)C=CH$_2$}] (17)

As discussed earlier, [Mo(CO)$_2$(η^5-C$_5$Me$_5$)(η^3-CH$_2$CHCHCH$_2$)] was reported[7,8] to react with a strong acid to give an η^4-vinylketene complex. In an attempt to apply this reaction to the isoelectronic complex (**17**), methanesulphonic acid was added to (**17**) in dichloromethane at -78°C. In the absence of any obvious reaction the mixture was warmed to room temperature and the solvent was evaporated in a stream of dinitrogen gas but only an intractable black oil was obtained after work-up and no identifiable molybdenum containing complex could be isolated. A proton NMR spectrum of complex (**17**) dissolved in trifluoroacetic acid showed no evidence of attack on the butadienyl ligand by the acid.

4.4.1.3 Reaction of triphenylphosphine with [MoCl(bipy)(CO)$_2${η^3-CH$_2$C(CO$_2$Et)C=CH$_2$}] (17)

Despite an 18 hour reflux in dichloromethane, followed by removal of this solvent and a further 12 hour reflux in boiling toluene, no reaction occurred between complex (**17**) and excess triphenylphosphine. Reaction between similar η^3-allyl molybdenum complexes and tertiary phosphines is known to occur under these conditions resulting in elimination

of allylphosphonium chloride and formation of a Mo(0) species[40], so more forcing conditions were not tried.

4.4.1.4 Reaction of dimethylmalonate anion with [MoCl(bipy)(CO)$_2${η^3-$CH_2C(CO_2Et)C=CH_2$}] (17)

No reaction between complex (**17**) and the anion of dimethylmalonate was observed even after an overnight reflux in toluene. Under similar conditions an analogous molybdenum η^3-allyl complex is readily attacked by the dimethylmalonate anion[41].

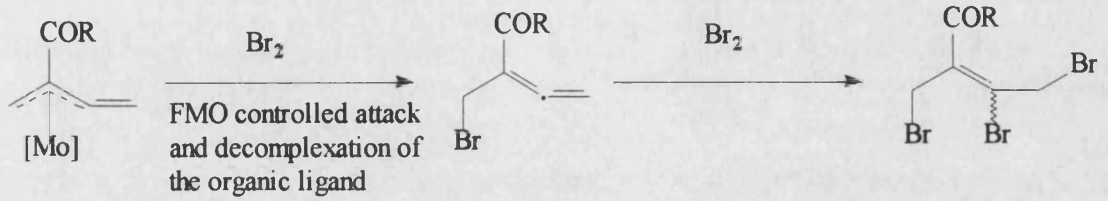
4.4.1.5 Conclusions from the reactions attempted on complexes (16), (17) and (18)

The EHMO calculations outlined previously on a model η^3-butadienyl complex closely related to complexes (**16**), (**17**) and (**18**) indicate that nucleophiles and electrophiles should attack the butadienyl ligand in the ways outlined previously in **Scheme 4.3.3**.

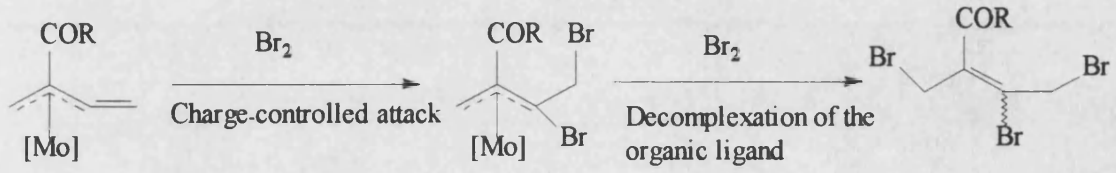
The reaction of molecular bromine with complexes (**16**), (**17**) and (**18**), giving the tribrominated organic products (**19**), (**20**) and (**21**) respectively, does not provide conclusive evidence that the electrophilic attack by Br_2 on the butadienyl ligand follows one particular pathway, as both FMO and charge-controlled attacks could yield the compounds obtained, as shown below (**Scheme 4.4.5**).

Scheme 4.4.5

Pathway (a):- FMO controlled attack

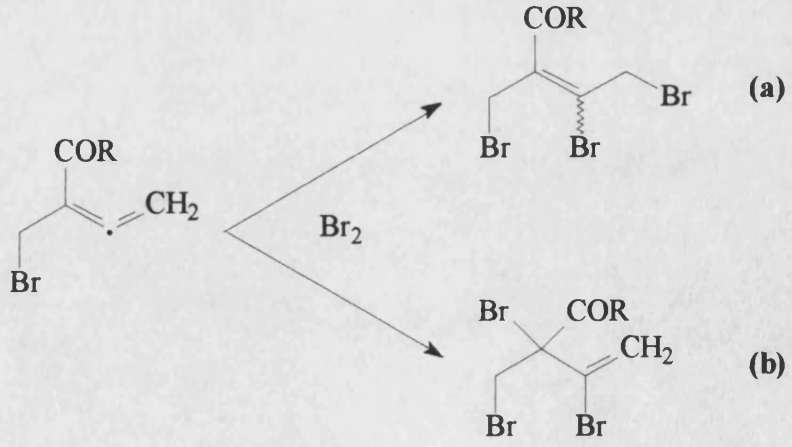


Pathway (b):- Charge-controlled attack



However, pathway **(a)** would be expected to lead to two products depending upon where the bromine attacks the decomplexed allene[42] (**Scheme 4.4.6**).

Scheme 4.4.6

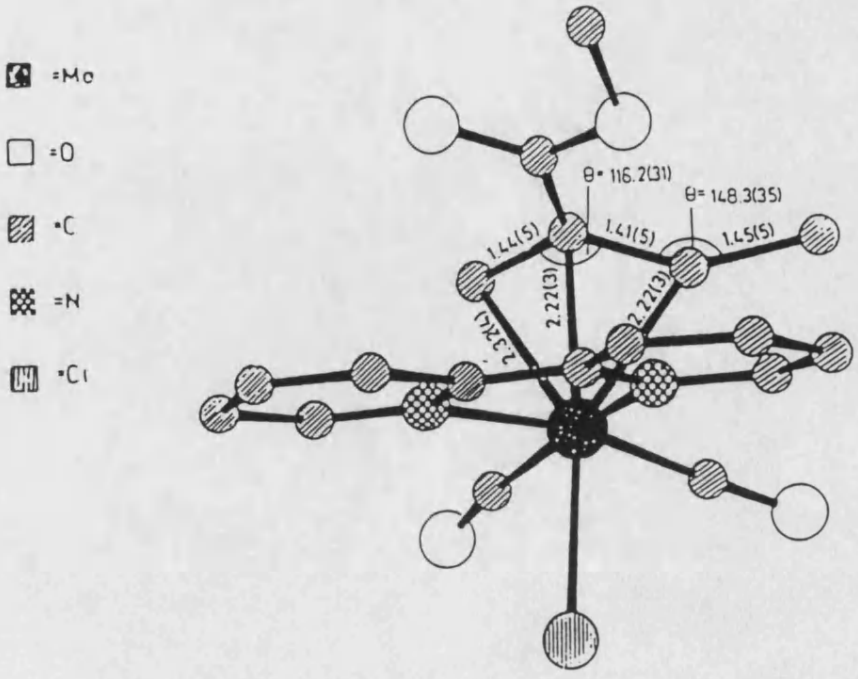


As no product **(b)** has been observed it may be that the charge-controlled pathway **(b)** is preferred. Another possibility is that initial decomplexation of the organic ligand occurs following oxidation of the metal centre with Br_2, and that subsequent bromination of the liberated butadiene yields the observed products.

The reaction of H^+ with complex (**17**) produced only a tar under forcing conditions from which no identifiable molybdenum species could be isolated, and it is likely that the acid simply caused the decomposition of (**17**). No reaction upon the η^3-butadienyl ligand was observed in NMR monitored reactions at ambient temperatures.

The conditions employed for nucleophilic attack on complex (**17**) are sufficient in the case of the analogous η^3-allyl complexes for reaction to occur with both neutral and charged species. The lack of reactivity of the η^3-butadienyl complex may be due to steric hindrance caused by the ester moiety on the C(2) atom, plus the bipyridyl ring system which together may prevent facile access to the organic ligand by the attacking species (**Figure 4.4.1**).

Figure 4.4.1



Thus, rather than pursue further reactions on an unreactive substrate it was of interest to investigate the reactivity of an analogous unsubstituted η^3-butadienyl complex and attempts made to prepare such species are discussed later in this thesis.

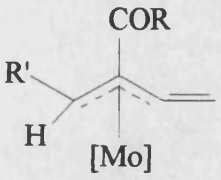
4.4.2 Attempts to prepare [MoCl(bipy)(CO)$_2${η^3-(Ph)CHC(CO$_2$Et)C=CH$_2$}]

In an attempt,

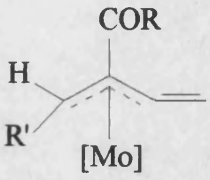
(i) to intercept an intermediate and,

(ii) to provide an insight into the mechanisms of formation of the substituted η^3-butadienyl complexes, it was decided to try to "label" with a bulky group the terminal carbon atom of the butadienyl ligand by the reaction of the $[MoCl(bipy)(CO)_3]^-$ anion (**15**) with a 1-substituted dichloro-2-butyne. Depending on the initial point of attack by (**15**) on the substituted dichloro-2-butyne, and the final conformation of the η^3-butadienyl ligand, four final products could conceivably be formed (**Scheme 4.4.7**).

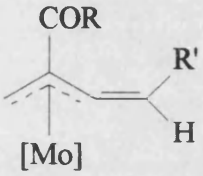
Scheme 4.4.7



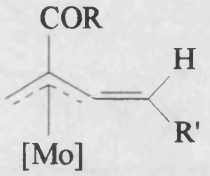
(a) *syn*



(b) *anti*



(c) *cis*



(d) *trans*

[Mo]=Mo(bipy)Cl(CO)$_2$

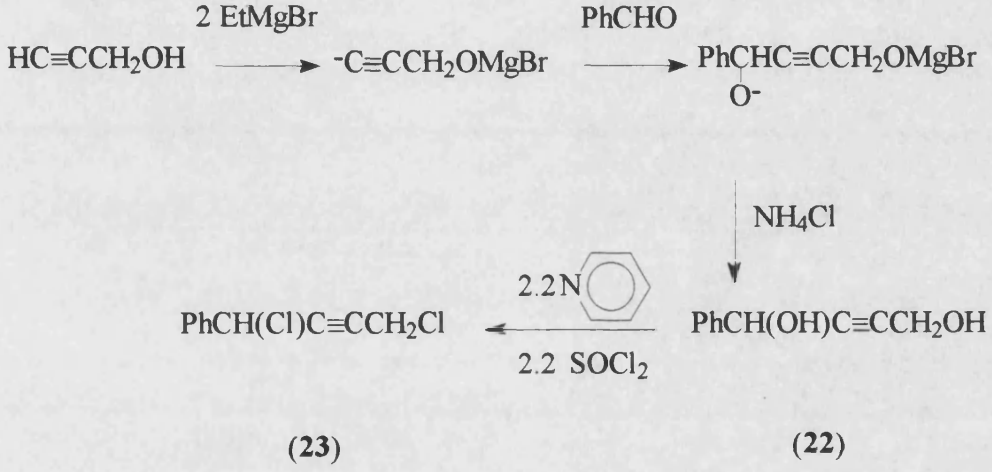
Thus **(a)** and **(b)** are formed by attack at the 2-position of R'CH(Cl)C≡CCH$_2$Cl and **(c)** and **(d)** by attack at the 3-position. In addition, the steric bulk of the substituent may help stabilise any σ-bonded intermediate involved in the formation of the η^3-butadienyl complex.

Initially, an attempt was made to prepare CH$_3$CH(Cl)C≡CCH$_2$Cl, but the precursor, CH$_3$CH(OH)C≡CCH$_2$OH, was found to decompose during purification by distillation, so the more stable solid compound PhCH(OH)C≡CCH$_2$OH (**22**) was prepared, and used to synthesise PhCH(Cl)C≡CCH$_2$Cl (**23**).

4.4.2.1 and 4.4.2.2 Preparation of $PhCH(OH)C{\equiv}CCH_2OH$ (22) and $PhCH(Cl)C{\equiv}CCH_2Cl$ (23)

Compounds (**22**) and (**23**) were prepared according to a general literature procedure[43] in 49% and 54% yields respectively (**Scheme 4.4.8**).

Scheme 4.4.8



(**23**) (**22**)

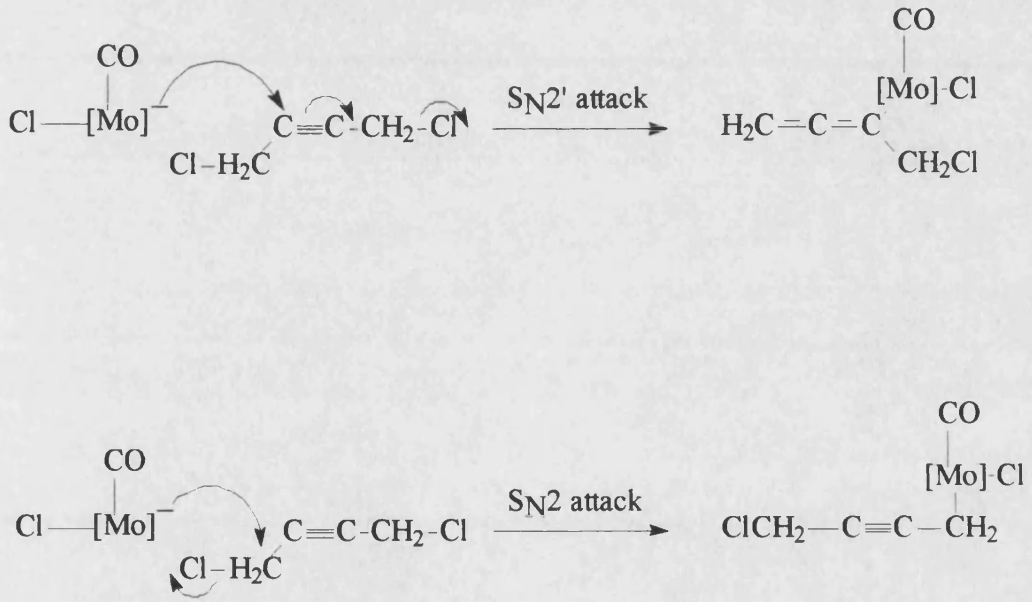
Unfortunately (**23**) was found to decompose quite quickly, possibly *via* polymerisation, presenting experimental complications in reactions involving Mo species. Thus reactions could only be performed using freshly prepared $PhCH(Cl)C{\equiv}CCH_2Cl$, which limited the scope of the investigation.

4.4.2.3 Reaction of $PhCH(Cl)C{\equiv}CCH_2Cl$ (23) with $Ph_4P[MoCl(bipy)(CO)_3]$ (15) in $EtOH/H_2O$

The reaction was performed by stirring the reactants together at low temperature (-78°C) and, after warming to room temperature, a light brown solid (**24**) was obtained.

The infra-red spectrum of complex (**24**) contained three carbonyl bands centred at 2000, 1950 and 1925cm^{-1} and no ester carbonyl was observed. Complex (**24**) was initially believed to be an intermediate in the overall methoxycarbonylation reaction. If the attack by the anionic complex (**15**) on the dichloro-2-butyne (**23**) was Sn2 rather than Sn2', as in the proposed mechanism, then the C≡C triple bond of the alkyne would still be intact and a tricarbonyl species would result (**Scheme 4.4.9**).

Scheme 4.4.9



[Mo]=Mo(bipy)(CO)$_2$

Attempts to record the Raman spectrum of complex (**24**), which would exhibit an intense C≡C triple bond stretching mode, were thwarted by decomposition of complex (**24**) in the Raman laser beam. The proton NMR spectrum of complex (**24**), which had only a low solubility, is extremely complex with the intensity of the aromatic region being

much greater than the expected 13 protons from the phenyl group and the 2,2'-bipyridyl ligand. This, along with an elemental analysis for complex (**24**) which was not in accord with that expected for a tricarbonyl intermediate of the type expected, indicated that the solid was not a single complex but a mixture of molybdenum species. The low solubility of the material together with limited stability prevented separation.

4.4.2.4 Reaction of complex (24) with pyridine

The mixture referred to above as complex (**24**) was treated with pyridine in THF in an attempt to generate an isolable complex. A dark red solid, complex (**25**), was obtained which proved to be a dicarbonyl species, with two C≡O absorptions in the infra-red spectrum centred at 1970 and 1900cm^{-1}, with the latter band showing a slight splitting. The proton NMR spectrum of complex (**25**), which again exhibited low solubility, exhibited intense signals in the aromatic region with the only other significant signals occurring as two doublets at δ3.55 and 2.66. The elemental analysis for complex (**25**) did not correspond to a realistic formulation so again it was not possible to identify a single component in what appeared to be a mixture of molybdenum species of low solubility.

4.4.2.5 Conclusions

The main problems encountered in this attempt to define the reaction sequence were,

(i) the rapid deterioration of the 1-phenyl-1,4-dichloro-2-butyne and

(ii) the lack of solubility in suitable solvents of the mixture of molybdenum complexes which were formed on reaction with this reagent.

Thus column separations were not possible and proton NMR spectra could only be obtained in deuterated DMSO, which appeared to react with the initial product so providing misleading data. The steric bulk of the substituted alkyne may indeed have prevented the formation of the expected η^3-butadienyl dicarbonyl complexes, and yielded a σ-bonded tricarbonyl molybdenum (II) species, but no conclusive evidence, other than solid-state infra-red data, is available to support this hypothesis.

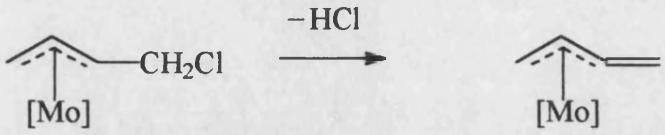
4.4.3 Attempts to prepare unsubstituted η^3-butadienyl molybdenum complexes

As discussed previously, the apparent lack of reactivity of the η^3-butadienyl ligand in complexes **(16)**, **(17)** and **(18)** may be in part due to the bulky C(2) substituent hindering the approach of nucleophilic or electrophilic reagents. Accordingly it was highly desirable to prepare a complex with an unsubstituted η^3-butadienyl ligand, particularly as the preparative routes for other transition metal η^3-butadienyl complexes also generally result in the formation of complexes with a high degree of substitution, as shown in **Section 4.1**.

Three possible routes to such analogues *via* oxidative addition to Mo(0) derivatives were explored:-

4.4.3.1 The abstraction of HCl from a chloromethyl substituted η^3-allyl complex (**Scheme 4.4.10**).

Scheme 4.4.10

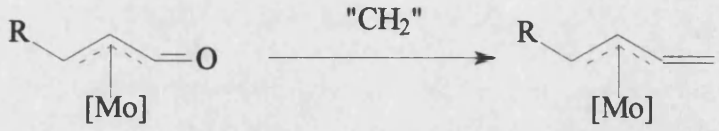


[Mo]=$MoCl(L_2)(CO)_2$; (L_2)=bipy, $(NCMe)_2$

The precursor complex could be made by the reaction of either $Ph_4P[MoCl(bipy)(CO)_3]$ (**15**) or $[Mo(bipy)(CO)_4]$ (**14**) with 1,4-dichloro-2-butene so giving $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2CHCHCH_2Cl\}]$. Since allyl derivatives of almost all transition metals are readily prepared, this route could provide a valuable general procedure for the preparation of a range of η^3-butadienyl complexes. The reaction of $[Mo(NCMe)_3(CO)_3]$ with 1,4-dichloro-2-butene in acetonitrile, which it was hoped would yield $[MoCl(NCMe)_2(CO)_2\{\eta^3\text{-}CH_2CHCHCH_2Cl\}]$, provides an alternative and versatile intermediate from which a series of complexes could be made. Both the *cis* and *trans*- isomers of 1,4-dichloro-2-butene and also 3,4-dichloro-2-butene, which could also give the desired complex, were subsequently employed in reactions with Mo(0) species.

4.4.3.2 A Wittig-type reaction on an η^3-oxoallyl complex (**Scheme 4.4.11**).

Scheme 4.4.11



[Mo]=Mo(bipy)Cl$(CO)_2$

[MoCl(bipy)$(CO)_2${η^3-(Ph)CHCHC=O}] can be prepared in excellent yield by the reaction between molybdenum hexacarbonyl, 2,2'-bipyridyl and cinnamoyl chloride[44]. A Wittig-type reaction on this complex would also reveal whether the terminal C=O group will react independently of the allyl system.

Attempts to prepare [MoCl(L_2)$(CO)_2${η^3-$CH_2CHCHCH_2Cl$}]
(L_2= bipy, $(NCMe)_2$)

4.4.3.1 Reactions of *cis* and *trans*-1,4-dichloro-2-butene with Ph_4P[MoCl(bipy)$(CO)_3$]

The reactions, carried out in dry methanol at low temperature (-10°C), gave with either isomer of 1,4-dichloro-2-butene a dark brown solid which was heavily contaminated with [Mo(bipy)$(CO)_4$]. The product (**26**), from the reaction employing the *cis*-isomer, had in its infra-red spectrum two carbonyl bands at 2000 and 1980cm^{-1}, whilst the product from the *trans*-isomer reaction appeared from infra-red evidence to produce a tricarbonyl product (**27**) with peaks at 2000, 1980 and 1935cm^{-1}. The proton NMR spectra of complexes (**26**) and (**27**) were not identical but in both the intensities of the aromatic signals were somewhat high due to contamination with [Mo(bipy)$(CO)_4$], and neither (**26**)

nor (**27**) yielded spectra compatible with the expected complex. It proved impossible to purify the products as they were not sufficiently soluble for column chromatography, and attempts to extract [Mo(bipy)$(CO)_4$] were also unsuccessful.

4.4.3.2 Reactions between *cis* and *trans*-1,4-dichloro-2-butene and [Mo(bipy)$(CO)_4$]

Similar products, (**28**) and (**29**), to those described above for the *cis*-isomer were obtained from both reactions. Products from both reactions appeared to be dicarbonyls with peaks at 2025 and 1950cm^{-1} in their infra-red spectra. The proton NMR spectra were also similar but were broad and poorly resolved, and the elemental analyses were not close to data expected for the desired complex. Again, attempts to purify these compounds were unsuccessful and it was subsequently decided to explore the following more promising route involving nitrile intermediates.

4.4.3.3 Reaction between *cis*-1,4-dichloro-2-butene and [$Mo(CO)_6$] in acetonitrile

After an overnight reflux a yellow powder (**30**) was obtained from this reaction which had no carbonyl band in the infra-red spectrum, but showed a weak ν(C≡N) stretch. As it reacted with 2,2'-bipyridyl to generate [$MoCl_4$(bipy)] it appears that [$MoCl_4(NCMe)_2$] was formed in this reaction, consequently less forcing conditions were sought.

4.4.3.4 Reaction between *cis*-1,4-dichloro-2-butene and [$Mo(NCMe)_3(CO)_3$]

A solution of [$Mo(NCMe)_3(CO)_3$] was first prepared by refluxing for 16h molybdenum hexacarbonyl in acetonitrile. After cooling to low temperature (-13°C), *cis*-1,4-dichloro-2-butene was added. Effervescence was immediately observed and a yellow

solid formed, complex (**31**), which proved to be a tricarbonyl species with three carbonyl bands at 2000, 1970 and 1955cm^{-1} in its infra-red spectrum and a weak C≡N stretch at 2300cm^{-1}. The proton NMR spectrum of complex (**31**) recorded in methanol-d^4 consisted of a multiplet at δ6.35 and two doublets at δ5.17 and 5.10, all three sets of peaks having the same intensity. A singlet peak at δ2.01 arose from NCMe being displaced from the complex by the NMR solvent. The elemental analysis of complex (**31**) corresponds quite closely to the formula $C_9H_9Cl_2MoNO_3$, however the proton NMR data do not correspond closely to the complex [MoCl(NCMe)(CO)$_3${η^3-$CH_2CHCHCH_2Cl$}] indicating that the complex may be unstable in solution. Attempts to purify complex (**31**) by recrystallisation were unsuccessful, as was an attempted elimination of HCl by treating complex (**31**) with sodium methoxide. Finally, attempts to generate a more soluble and stable derivative, by treating complex (**31**) with bidentate phosphines or 2,2'-bipyridyl failed to yield tractable solids.

Attempts to prepare [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=CH$_2$}]

4.4.3.5 Preparation of [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (32)

Complex (**32**) was prepared in 90% yield from the reaction of [Mo(CO)$_6$], 2,2'-bipyridyl and cinnamoyl chloride in refluxing THF. Complex (**32**) gave satisfactory elemental analyses without further purification and was found to contain two ν(C≡O) bands at 1965 and 1900cm^{-1} as well as a ν(C=O) band at 1730cm^{-1}. As complex (**32**) is only partially soluble even in highly polar solvents such as DMSO and DMF, ^{1}H NMR data were unavailable.

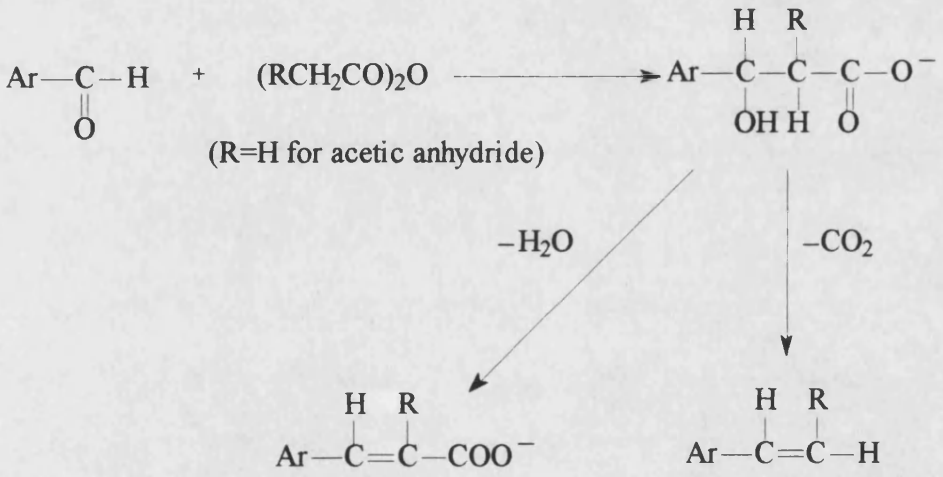
4.4.3.6 Reaction of [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (32) with Ph_3P^+-CH_2^-

The phosphorus ylid was prepared in DMSO, in which complex (**32**) is slightly soluble, from methyltriphenylphosphonium bromide according to literature procedure[45]. Complex (**32**) was added to the ylid but the only identifiable product obtained was [Mo(bipy)$(CO)_4$].

4.4.3.7 Attempted Perkin reaction on [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (32)

Aromatic aldehydes condense with anhydrides to give either α, β-unsaturated acids by dehydration, or alkenes by decarboxylation, *via* the intermediacy of an initial β-hydroxy acid salt (**Scheme 4.4.12**)

Scheme 4.4.12



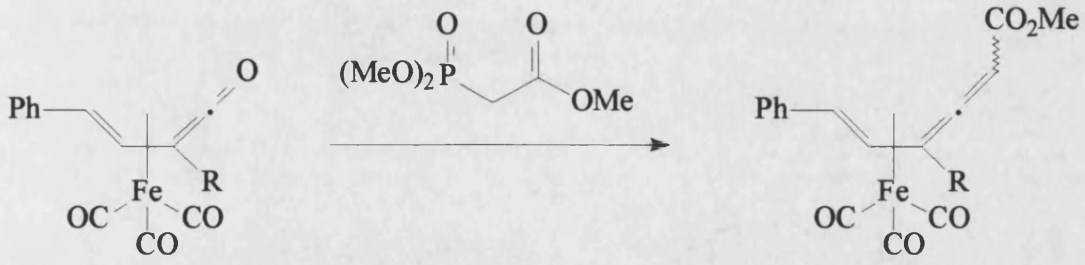
This procedure is known as the Perkin reaction[46,47] and an attempt was made to apply it to complex (**32**) in order to produce an η^3-butadienyl complex. Complex (**32**) was

heated for 1 hour in refluxing acetic anhydride containing lead(II) oxide and glacial acetic acid, according to literature procedures[48], and the mixture then stirred at room temperature. After this time the only solid isolated exhibited no carbonyl bands in its infra-red spectrum and it appears that complex (**32**) decomposed during the vigorous reaction.

4.4.3.8 Reaction of [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (32) with the anion of trimethylphosphonoacetate

An iron tricarbonyl complex [Fe(CO)$_3${η^4-(Ph)CH=CHC(Me)=C=O}] has been reported[49] to yield [Fe(CO)$_3${η^4-(Ph)CH=CHC(Me)=CHCHCO$_2$R}] (R=Me, ^{t}Bu) following treatment of the vinylketene with the anion of *tert*-butyldiethylphosphonoacetate (R=^{t}Bu) or trimethylphosphonoacetate (R=Me) (**Scheme 4.4.13**), and an attempt was made to form the η^3-butadienyl complex [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=CHCO$_2$Me}] following an analogous procedure.

Scheme 4.4.13



R=Me, Bu, ^{t}Bu

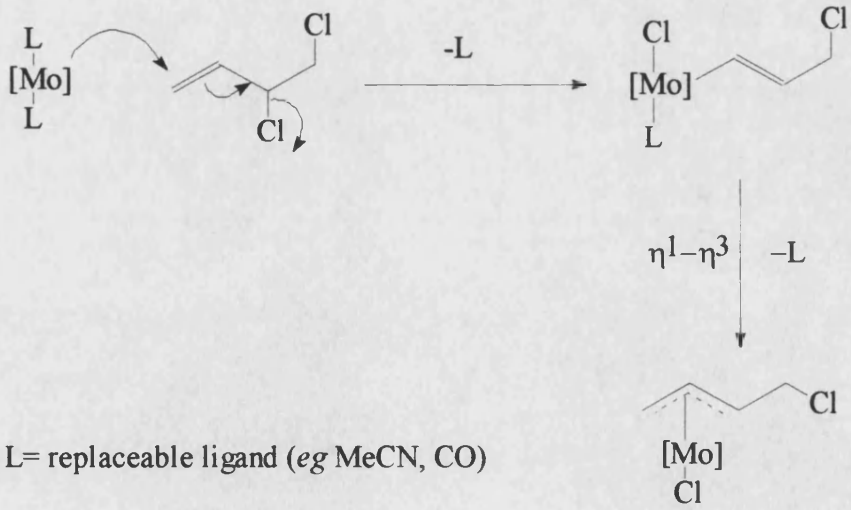
Accordingly the anion of trimethylphosphonoacetate was generated *in situ* using sodium hydride, and complex (**32**) then added. After stirring for 20h only

[Mo(bipy)$(CO)_4$] and a small amount of unreacted (**32**) were present in the reaction mixture.

4.5 Preparation of [$MoCl_2(NCMe)(CO)_2(\eta^4$-$CH_2$=CH-CH=$CH_2$)] (33)

As discussed earlier, attempts were made to prepare the complexes [$MoCl(L)_2(CO)_2\{\eta^3$-$CH_2CHCHCH_2Cl\}$] (L_2=$(NCMe)_2$, bipy) *via* the reaction of *cis* or *trans*-1,4-dichloro-2-butene with various Mo(0) derivatives. As these attempts proved to be unsuccessful, and as the preparation of such a complex could lead to an important, general route to transition metal η^3-butadienyl complexes by abstraction of HCl, the reaction of the isomeric alkene, 3,4-dichloro-1-butene, with Mo(0) complexes was next explored. Such a reaction would be expected to lead to the formation of the desired complex as shown in **Scheme 4.5.1**.

Scheme 4.5.1



L= replaceable ligand (*eg* MeCN, CO)

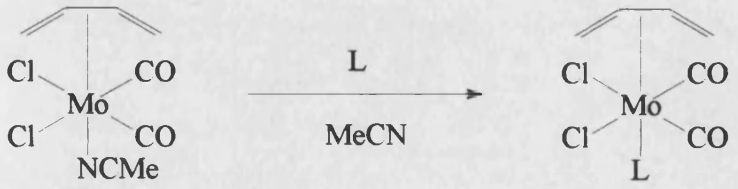
Accordingly, a solution of $[Mo(NCMe)_3(CO)_3]$ was prepared by refluxing $[Mo(CO)_6]$ in acetonitrile for 2.5h. The solution was then cooled in ice to 0°C and a two-fold excess of 3,4-dichloro-1-butene added dropwise. Effervescence occurred during the addition, and the reaction solution was observed to darken in colour from pale yellow to a deep orange. After stirring at room temperature for ~1h a yellow precipitate formed which was subsequently filtered off following overnight refrigeration of the reaction mixture. The yellow solid (**33**) thus obtained was washed with a 10:1 (v:v) solution of diethyl ether/acetonitrile and dried under suction. The infra-red spectrum of complex (**33**), obtained as a Nujol mull, was found to contain a $\nu(C\equiv N)$ stretch at $2313cm^{-1}$ whilst $\nu(C\equiv O)$ bands were present at 2015, 2004, 1952 and $1935cm^{-1}$. An infra-red spectrum obtained as an acetonitrile solution showed complex (**33**) to be a dicarbonyl species, with the four CO bands previously observed coalescing into two peaks centred at 2022 and $1952cm^{-1}$. The ^1H NMR spectrum of complex (**33**) was obtained in CD_3CN and exhibited a broad singlet peak at δ6.41 and a broad multiplet at δ6.28 together with doublets at δ5.11 and 4.99 and a singlet signal at δ2.32. These peaks were in the approximate ratio of 1:2:2:2:20 protons respectively. Elemental analysis for complex (**33**) revealed that only one of the expected two NCMe ligands was in fact present. The analysis corresponded closely to that expected for a complex of molecular formula $C_8H_9Cl_2MoNO_2$. Other than a 16-electron species, the most likely structure for complex (**33**) based on the above data appears to be an η^4-butadiene derivative $[Mo(NCMe)Cl_2(CO)_2(\eta^4\text{-}CH_2CHCHCH_2)]$. Such a complex would fit the ^1H NMR data reported above tolerably well. The protons of the terminal $=CH_2$ groups would be split by the adjacent =CH protons into the two doublets found at δ5.11 and 4.99 with the =CH moieties themselves appearing as the two proton multiplet resonating at δ6.28. Although the signal at δ2.32 in the ^1H NMR spectrum of (**33**) is far more intense than the three proton singlet peak expected for the single NCMe ligand of the complex, this is almost certainly due to protons in the deuterated solvent. However, the structure of

complex (**33**) cannot be assigned unequivocally to that proposed as there is an unexplained one proton singlet peak at δ6.41 present in the ^{1}H NMR spectrum . Other than the highly polar DMSO an DMF in which the complex appears to decompose, complex (**33**) is only soluble in acetonitrile and attempts to grow crystals suitable for an X-ray study from this medium were unsuccessful. As the proposed structure of complex (**33**) could be a novel and potentially interesting one if corroborated the following discussion concerns the attempts made to prepare a more soluble derivative upon which an X-ray crystallographic study could be made.

Reactions of complex (33) with potential monodentate ligands

As complex (**33**) appears to contain only one replaceable NCMe ligand, the following reactions were performed to replace this with other monodentates such as phosphines or pyridine derivatives as shown in **Scheme 4.5.2**.

Scheme 4.5.2



Complex (1)

L=monodentate phosphine (*eg* triphenylphosphine) or nitrogen donor ligand (*eg* pyridine)

4.5.2 Reaction of complex (33) with triphenylphosphine

A solution of one equivalent of triphenylphosphine dissolved in dichloromethane was added, dropwise with stirring, to complex (**33**) in acetonitrile. After stirring for 0.2h, an infra-red spectrum was taken of the reaction mixture which showed the presence in solution of a dicarbonyl species with ν(C≡O) bands at 1939 and 1829cm^{-1} (*cf* 2022 and 1952cm^{-1} for complex (**33**)). Removing the reaction solvents *in vacuo* left a dark-orange solid. Attempts to recrystallise this material from a variety of solvent systems, including a chloroform/cyclohexane mixture, xylene or diethyl ether and acetonitrile/cyclohexane all proved to be unsuccessful. The crude solid had ν(C≡O) bands at 1921 and 1817cm^{-1} together with a weaker band at 2033cm^{-1} present in its infra-red spectrum. The elemental analysis obtained was not close to that expected. Thus, it appears that the material obtained from this reaction is a mixture of two or more complexes. Given the size of the triphenylphosphine molecule, it is possible that steric hindrance is preventing the successful outcome of this reaction, consequently less bulky phosphines were used with complex (**33**) as discussed below.

4.5.3 Reaction of complex (33) with methyldiphenylphosphine

A stirred solution of complex (**33**) in acetonitrile was treated dropwise with one equivalent of methyldiphenylphosphine. After stirring at room temperature for 0.2h, an infra-red spectrum was taken of the reaction mixture which indicated the presence in solution of a dicarbonyl species with ν(C≡O) bands at 1927 and 1825cm^{-1}. The volume of solvent was then reduced by approximately two-thirds and the reaction mixture refrigerated overnight. Precipitation appeared to have been induced by this treatment but upon filtration only an intractable dark-brown oil was obtained.

4.5.4 Reaction of complex (33) with dimethylphenylphosphine

The procedure outlined above was repeated using dimethylphenylphosphine. Again, infra-red spectroscopy detected the presence in solution of a dicarbonyl species with $\nu(C\equiv O)$ bands at 1935 and 1838cm^{-1}. However, reduction of the solvent volume and overnight refrigeration only led to the recovery of an intractable dark-brown tar.

4.5.5 Reaction of complex (33) with pyridine

A few drops of neat pyridine were added to a solution of complex (**33**) in acetonitrile. After stirring at room temperature for 0.2h, a sandy-yellow precipitate was formed which was filtered off, washed with diethyl ether and dried under suction to give complex (**34**). The infra-red spectrum of complex (**34**) contained two $\nu(C\equiv O)$ bands centred at 1919 and 1817cm^{-1}. The ^1H NMR spectrum of complex (**34**) was obtained in DMSO-d^6 and exhibited a broad singlet at δ8.75 and multiplets at δ8.17 and 7.70 with intensities of 2:1:2 respectively, these corresponding to the pyridine protons. A multiplet was found at δ6.35 along with doublet signals at δ5.28 and 5.15, with relative intensities of ~0.4:0.5:0.5 protons. This indicates that more than one pyridine group has been incorporated into the complex. The elemental analysis of complex (**34**) corresponds quite closely to that expected for the complex $[MoCl_2(C_5H_5N)_2(CO)_2(\eta^2\text{-}CH_2{=}CH\text{-}CH{=}CH_2)]$ in which the NCMe ligand has been replaced by pyridine and the η^4-butadiene ligand has been converted to an η^2-type moiety thus allowing the second pyridine molecule to be incorporated. However the ^1H NMR spectrum did not show the expected intensity ratios (*four* pyridine ligands were indicated per butadiene ligand showing that complex (**34**) has undergone partial decomposition in the NMR solvent) and as complex (**34**) is only soluble in highly polar solvents such as DMSO or DMF no suitable crystals for an X-ray crystallographic investigation could be

obtained. Consequently an acetonitrile solution of complex (**33**) was reacted with 2-methoxypyridine in an attempt to prepare a more soluble complex. In this case however only a non-carbonyl containing solid was isolated whose infra-red and microanalytical data indicated that $[MoCl_3(NCMe)_3]$ had been formed instead, possibly by a disproportionation reaction.

Reactions upon the η^4-butadiene ligand of complex (33)

4.5.6 Reaction of complex (33) with 1,4-diphenyl-1,3-butadiene

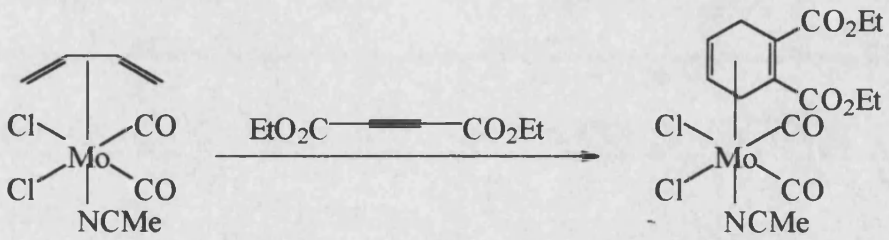
As the reaction above appeared to indicate that the η^4-butadiene ligand thought to be present in complex (**33**) could be easily converted to an η^2-butadiene, it was hoped that treatment of (**33**) with 1,4-diphenyl-1,3-butadiene would lead to the total replacement of the original ligand and that a complex of the type $[MoCl_2(NCMe)(CO)_2(\eta^4\text{-PhCH=CH-CH=CHPh})]$, which would be more soluble than complex (**33**) could be prepared.

Accordingly, complex (**33**) was dissolved in acetonitrile and was treated with a solution of 1,4-diphenyl-1,3-butadiene in toluene. No reaction appeared to occur at room temperature but after heating the reaction mixture under reflux for 0.6h, an infra-red spectrum showed the presence in solution of a dicarbonyl species possessing $\nu(C\equiv O)$ bands at 1919 and 1798cm^{-1}. The reaction solvent was then reduced to about one-third of the original amount and the reaction mixture refrigerated overnight. Only a small of non-carbonyl containing material was subsequently obtained however, and further treatment of the filtrate did not yield any more solid. It would appear that decomposition of the carbonyl species had occurred.

4.5.7 Reaction of complex (33) with diethylacetylenedicarboxylate

By treating complex (**33**) with diethylacetylenedicarboxylate, it was hoped that a Diels-Alder type reaction could be induced to occur upon the η^4-butadiene ligand leading to the complex shown below in **Scheme 4.5.3**, which would be likely to be more soluble than the original complex.

Scheme 4.5.3



Accordingly, a solution of complex (**33**) in acetonitrile was treated with diethylacetylenedicarboxylate. Infra-red spectra were taken of the reaction mixture after 2, 3 and 4h stirring at room temperature; all showed the presence in solution of several carbonyl-containing species with bands at 2027 (weak), 1987, 1948 (weak), 1825 and 1800 (weak)cm^{-1}. Reduction of the solvent volume by half and refrigeration of the reaction solution yielded only a non-carbonyl containing solid and no further material could be isolated from the reaction filtrate.

4.5.8 Reaction of complex (33) with diphenylacetylene

The above procedure was repeated using diphenylacetylene. The colour of the reaction solution changed to a darker orange-brown over ~2h. An infra-red spectrum taken at this point exhibited carbonyl bands at 2081, 2014 and 1950cm^{-1}. After removing the reaction solvent *in vacuo*, the brown residue was redissolved in dichloromethane and cyclohexane was added. Following overnight refrigeration, a small amount of solid was filtered off, but this proved to be a mixture of several Mo carbonyl species and it was not possible to isolate a single complex.

4.5.9 Reaction of complex (33) with bromine

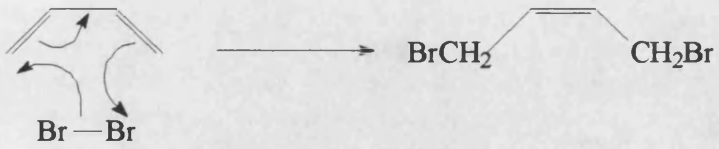
In an attempt to brominate the η^4-butadiene ligand thought to be present in complex (**33**) and thus isolate a compound which could be identified as having arisen from such a reaction, complex (**33**) was dissolved in acetonitrile and cooled to -40°C before being treated with 3.0 equivalents of molecular bromine. The reaction mixture was allowed to warm to room temperature over ~2 hours then filtered through florisil to remove the oxidised inorganic residues. Column chromatography on silica using 4:1 60-80° petroleum ether/ethyl acetate as eluant yielded a yellow oil (**35**). The ^{1}H NMR spectrum of (**35**), obtained in $CDCl_3$, showed that (**35**) was a mixture of two isomers in a 2:1 ratio. The more abundant isomer has a 4 proton double doublet at δ3.94 (J=1.8, 5.5Hz) and a 2 proton multiplet at δ5.80 with the less abundant isomer exhibiting similar signal patterns at δ3.87 (dd, J=2.2, 4.4Hz) and δ5.88 (m) at exactly half the intensities. The ^{1}H NMR spectrum of (**35**) is remarkably similar to that for *cis*-1,4-dichloro-2-butene which was obtained in order to determine the purity of a commercial sample (*cis*-1,4-dichloro-2-butene has a two proton multiplet at δ5.78 and a four proton double doublet at δ4.10 (J=1.8, 5.3Hz) in it's ^{1}H NMR spectrum (obtained in $CDCl_3$)). It is pertinent to note

that 1,4-dibromo-2-butene has been prepared by the bromination of butadiene[51]. Thus it appears that (**35**) is a mixture of the *cis* and *trans*- isomers of 1,4-dibromo-2-butene although it is not clear from the ^{1}H NMR spectrum whether the *cis*- or *trans*-isomer is the more abundant. The ^{13}C NMR spectrum of (**35**) would appear to confirm this with two sets of alkene carbon resonances appearing at δ130.76, 129.79, 129.69 and 129.63 along with four $\underline{C}H_2Br$ signals at δ37.80, 33.70, 30.85 and 24.47, these assignments being confirmed as CH and CH_2 signals respectively by a 135DEPT spectrum (*cf cis*-1,4-dichloro-2-butene which has alkene carbon resonances at δ129.56 and a $\underline{C}H_2$ signal at δ37.90 in it's ^{13}C NMR spectrum). The mass spectrum of (**35**) had M^{+}=213 with the 1:2:1 pattern characteristic of a dibrominated species, some tribrominated material was also present which accounts for the inaccuracy of the microanalysis obtained.

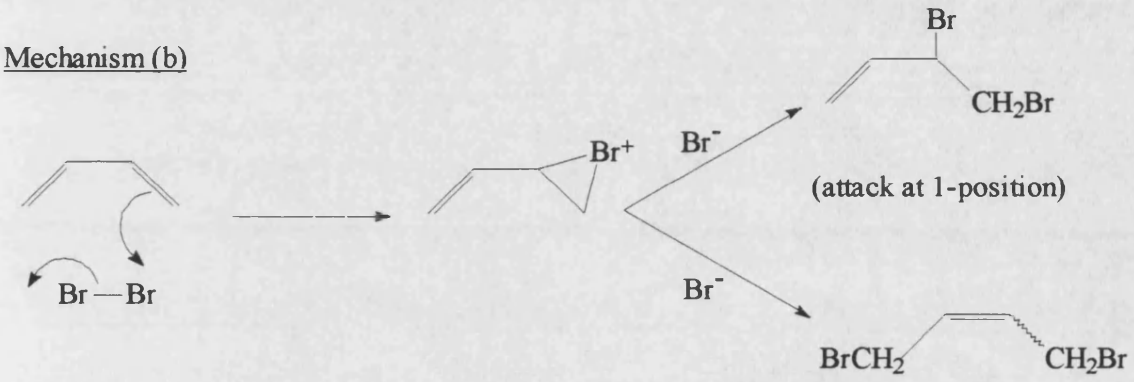
The mechanism of formation of *cis* and *trans*-1,4-dibromo-2-butene from complex (**33**) is unclear; the expected, concerted mechanism (**a**) shown below in **Scheme 4.5.4**, would only give one isomer (the *trans*-isomer) as it would occur instantaneously. If mechanism (**b**), involving a cyclic bromonium ion, were followed then *cis* and *trans*-isomers could be formed but there would be 1,2-dibromo-2-butene formed also and this was not observed in the reaction products. It is possible that complex (**33**) exists in two conformations which could thus give rise to the two observed isomer products termed (**35**).

Scheme 4.5.4

Mechanism (a)



Mechanism (b)



4.5.10 Attempted preparation of $[MoCl_2(CNPr)(CO)_2(\eta^4\text{-}CH_2{=}CH\text{-}CH{=}CH_2)]$

In an attempt to prepare the PrCN substituted analogue of complex (**33**), a similar procedure was followed to that outlined above but employing PrCN as solvent. No precipitation occurred following the addition of the 3,4-dichloro-1-butene, and the reaction mixture was refrigerated. After about a week's refrigeration, yellow crystals admixed with $[Mo(CO)_6]$ were observed in the reaction flask. On isolation, the yellow crystals proved to be suitable for an X-ray crystallographic study, and were found to be $[MoCl_3(NCPr)_3]$ (**36**), arising probably as a result of disproportionation and subsequent oxidation during the reaction. The structure of this complex is discussed below.

THE CRYSTAL STRUCTURE OF $[MoCl_3(NCPr)_3]$ (36)

Figure 4.5.1 overleaf shows an ORTEP view of complex (**36**) along with the atomic numbering scheme employed whilst **Table 4.5.1** below summarises the bond lengths and selected bond angles in the complex.

An X-ray crystallographic study of $[MoCl_3(NCMe)_3]$.MeCN was reported by Roh and Bruno[52] but partial occupation of the site by the lattice MeCN molecule meant that the structure could not be sufficiently refined to allow the calculation of bond lengths and angles, however the complex was assigned as having a *meridional*-octahedral geometry about the metal as observed in the structure of complex (**36**).

Figure 4.5.1

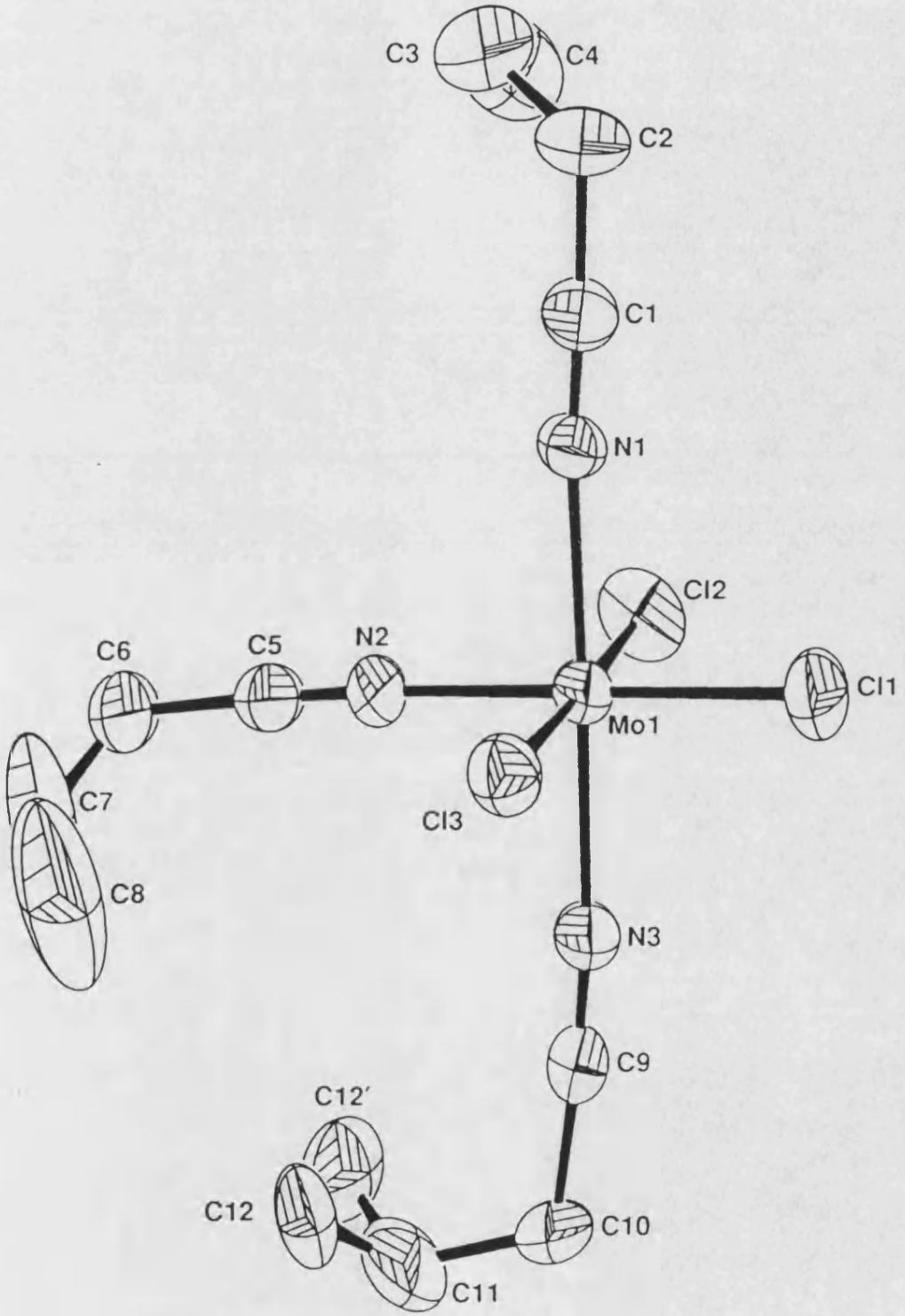


Table 4.5.1

Bond	Length (Å)	Bond	Length (Å)
Mo-Cl(1)	2.368(4)	C(6)-C(7)	1.409(15)
Mo-Cl(2)	2.391(4)	C(7)-C(8)	1.182(17)
Mo-Cl(3)	2.399(4)	C(9)-C(10)	1.496(11)
Mo-N(1)	2.128(8)	C(10)-C(11)	1.542(16)
Mo-N(2)	2.144(7)	C(11)-C(12)	1.360(37)
Mo-N(3)	2.120(8)	C(11)-C(12')	1.236(20)
C(1)-C(2)	1.480(11)	C(1)-N(1)	1.123(8)
C(2)-C(3)	1.526(13)	C(5)-N(2)	1.113(8)
C(3)-C(4)	1.443(15)	C(9)-N(3)	1.118(9)
C(5)-C(6)	1.492(11)		

Bond	Angle (°)	Bond	Angle (°)
Cl(2)-Mo-Cl(1)	92.0(2)	N(3)-Mo-N(1)	177.9(2)
Cl(3)-Mo-Cl(2)	174.8(1)	C(1)-N(1)-Mo	172.5(6)
N(1)-Mo-Cl(1)	89.7(2)	C(2)-C(1)-N(1)	176.9(8)
N(2)-Mo-Cl(1)	179.6(1)	C(3)-C(2)-C(1)	110.6(8)
N(2)-Mo-N(1)	90.6(3)		

Conclusions

Although the primary objective of developing a general route to transition metal η^3-butadienyl complexes was not realised, the preparation of $[MoCl_2(NCMe)(CO)_2(\eta^4\text{-}CH_2{=}CH\text{-}CH{=}CH_2)]$ has provided an interesting and potentially synthetically useful new complex. Despite not being able to establish unequivocally the structure of this complex by crystallography, it seems highly likely that complex **(33)** has the structure proposed given the results of the bromination reaction. Unfortunately, time constraints prevented further work in this area but the results obtained make it probable that complex **(33)** has the assigned structure.

4.6 EXPERIMENTAL

The complexes $[Mo(bipy)(CO)_4]$ **(14)**[36], $Ph_4P[MoCl(bipy)(CO)_3]$ **(15)**[37], $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2\}]$ **(16)**[25], $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CO_2Et)C{=}CH_2\}]$ **(17)**[25, 26] and $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CONHEt)C{=}CH_2\}]$ **(18)**[27-29] were prepared according to published methods in 98%, 95%, 49%, 38% and 52% yield respectively. An example of the general method of preparation for the η^3-butadienyl complexes is given below.

Preparation of $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CO_2Et)C{=}CH_2\}]$ (17)

A stirred solution of $PPh_4[MoCl(bipy)(CO)_3]$ (2.00g, 2.81mmol) in 30:1 (v:v) ethanol/water ($31cm^3$) was cooled to below -10°C and 1,4-dichloro-2-butene ($0.35cm^3$, 3.58mmol) added. After stirring at less than -10°C for 1h, then at room temperature for a further 1h, the resulting red mixture was filtered and the red crystalline solid thus obtained washed first with ethanol ($30cm^3$) followed by 40-60° petroleum ether ($30cm^3$) and then dried to give complex **(17)**.

Yield=0.50g (38%)

Infra-red: $\nu(C{\equiv}O)$ 1970, 1895cm^{-1}; $\nu(C{=}O)$ 1685cm^{-1}

NMR (^1H, CD_2Cl_2, 270MHz): δ8.88-7.51 (8H, m); 6.28 (1H, d, J=2.2Hz); 5.66 (1H, d, J=2Hz); 3.65 (1H, s); 3.27 (1H, qd, J=7.1, 10.3Hz); 3.12 (1H, qd, J=7.1, 10.3Hz); 1.96 (1H, s); 0.65 (3H, t, J=7.1Hz)

Microanalysis: Found; C, 46.8; H, 3.52; N, 5.81%. Calculated for $C_{19}H_{17}ClMoN_2O_4$; C, 48.68; H, 3.65; N, 5.98%

4.6.1 Reactions on [MoCl(bipy)(CO)$_2${η^3-$CH_2C(COR)C=CH_2$}] (R=OMe (16), OEt (17), NHEt (18))

4.6.1.1 General bromination procedure

To the ester complexes (**16**) or (**17**) or the amide complex (**18**) in dichloromethane at -78°C was added 2.1 equivalents of molecular bromine in dichloromethane over 0.3-0.5h. The reaction mixture was allowed to warm to room temperature over 3h then filtered through florisil and column chromatographed on silica using dichloromethane as eluant to give either yellow oils (from complexes (**16**) and (**17**)) or a white solid (from complex (**18**)).

Product:- $BrCH_2C(CO_2Me)=C(Br)CH_2Br$ (19)

Yield=43%

Infra-red: ν(C=O) 1720cm^{-1}; ν(C=C) 1600cm^{-1}

NMR (^{1}H, $CDCl_3$, 270MHz): δ4.84 (2H, s); 4.42 (2H, s); 3.88 (3H, s)

NMR (^{13}C, $CDCl_3$, 68MHz): δ163.4 (C=O); 141.1, 132.2 (C=C); 53.1 (CH_2Br); 34.5 (CH_2Br); 31.6 (CH_3)

Microanalysis: Found; C, 22.0; H, 2.14; N, 0%. Calculated for $C_6H_7Br_3O_2$; C, 20.70; H, 2..03; N, 0%.

Mass spec.: M^+=351 (tribrominated)

Product:- $BrCH_2C(CO_2Et)=C(Br)CH_2Br$ (20)

Yield=50%

Infra-red: ν(C=O) 1710cm^{-1}; ν(C=C) 1600cm^{-1}

NMR (^{1}H, $CDCl_3$, 270MHz): δ4.82 (2H, s); 4.42(2H, s); 4.34 (2H, q, J=7.1Hz); 1.38 (3H, t, J=7.1Hz)

NMR (^{13}C, $CDCl_3$, 68MHz): δ163.0 (C=O); 140.3, 132.6 (C=C); 62.4 ($CO_2CH_2CH_3$); 34.6 (CH_2Br); 31.7 (CH_2Br); 14.01 ($CO_2CH_2CH_3$)

Microanalysis: Found; C, 24.2; H, 2.47; N, 0%. Calculated for $C_7H_9Br_3O_2$; C, 23.04; H, 2.49; N, 0%

Mass spec: M^+=365 (tribrominated)

Product:- $BrCH_2C(CO_2NHEt)=CCH_2Br$ (21)

Yield=18%

Infra-red: ν(N-H) 3260cm^{-1}; ν(C=C) 1630cm^{-1}; ν(C=O) 1540cm^{-1}

NMR (^1H, $CDCl_3$, 270MHz): δ6.14 (1H, br s); 4.42 (1.8H, s); 4.31 (0.2H, s); 4.28 (2H, s); 3.44 (2H, dq, J=5.9, 7.3Hz); 1.26 (3H, t, J=7.3Hz)

NMR (^{13}C, $CDCl_3$, 68MHz): δ35.7, 35.1, 33.02, 31.8, 28.5 (all CH_2 signals); 14.5 (CH_3)

Microanalysis: Found; C, 23.4; H, 2.83; N, 3.83%. Calculated for $C_7H_{10}Br_3NO$; C, 23.11; H, 2.77; N, 3.85%

Mass spec: M^+=364 (tribrominated)

4.6.1.2 Reaction of methanesulphonic acid with $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CO_2Et)C=CH_2\}]$ (17)

A stirred solution of $[MoCl(bipy)(CO)_2\{\eta^3\text{-}CH_2C(CO_2Et)C=CH_2\}]$ (**17**) (0.25g, 0.52mmol) in dichloromethane (10cm^3) was cooled to -78°C and a few drops of methanesulphonic acid added. After 3h at less than -70°C a few more drops of the acid were added and the reaction allowed to warm to room temperature. The solvent was then removed by evaporation in a stream of dinitrogen gas to leave a black, intractable tar. Any excess acid present was removed with an aqueous solution of $NaHCO_3$ but no identifiable molybdenum containing material could be isolated.

4.6.1.3 Reaction of triphenylphosphine with [MoCl(bipy)(CO)$_2${η^3-CH$_2$C(CO$_2$Et)CH$_2$}] (17)

Complex (17), [MoCl(bipy)(CO)$_2${η^3-CH$_2$C(CO$_2$Et)C=CH$_2$}] (0.10g, 0.21mmol) was dissolved in dichloromethane (5cm^3) and triphenylphosphine (70mg, 0.27mmol) added. After stirring at room temperature for 1.75h, the mixture was heated under reflux for 18h. No reaction had occurred so the solvent was removed and toluene (5cm^3) added. However, even after 12h reflux in the higher boiling solvent, only the starting materials were present.

4.6.1.4 Reaction of dimethylmalonate anion with [MoCl(bipy)(CO)$_2${η^3-CH$_2$C(CO$_2$Et)CH$_2$}] (17)

Dimethylmalonate (0.03cm^3, 0.23mmol) was added to a 60% sodium hydride/mineral oil dispersion (0.01g, 0.25mmol) in toluene (3cm^3) and the mixture heated at 45-55°C for 0.75h. After cooling to room temperature, complex (**15**) (0.10g, 0.21mmol) was added and the reaction mixture heated at 45°C for 5h then refluxed overnight. No reaction occurred under these conditions.

4.6.2 Attempts to prepare [MoCl(bipy)(CO)$_2${η^3-(Ph)CHC(CO$_2$Et)C=CH$_2$}]

4.6.2.1 Preparation of PhCH(OH)C≡CCH$_2$OH (22)

A solution of ethylmagnesium bromide was prepared in THF (250cm^3) from magnesium turnings (12.13g, 0.51mol) and bromoethane (37.70cm^3, 0.51mol) and was cooled to below 0°C, prior to adding, over 0.75h, a solution of propargyl alcohol

(14.70cm^3, 0.25mol) in THF (150cm^3) *via* an addition funnel. The reaction mixture was stirred at room temperature for 1h then cooled back down to 0°C and benzaldehyde (25.82cm^3, 0.25mol) added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for a further 48h before being cooled, and saturated aqueous ammonium chloride added to destroy any remaining Grignard reagent. After filtration through celite and isolation with diethyl ether, the combined organic layers were dried (sodium sulphate), filtered and evaporated *in vacuo* to give a brown oil to which carbon tetrachloride was added. After refrigeration, two crops of **(22)** as a pale yellow solid were obtained.

Yield=20.12g (49%)

NMR (^{1}H, $CDCl_3$, 270 MHz): δ7.53-7.25 (5H, m); 5.44 (1H, s); 4.25 (2H, s)

NMR (^{13}C, $CDCl_3/CD_3OD$, 68MHz): δ140.5, 128.1, 127.8, 126.3 (aromatics); 84.7, 84.1 (C≡C); 63.5 (CH); 49.9 (CH_2)

Microanalysis: Found; C, 74.3; H, 6.18; N, 0%. Calculated for $C_{10}H_{10}O_2$; C, 74.06; H, 6.21; N, 0%

4.6.2.2 Preparation of PhCH(Cl)C≡CCH$_2$Cl (23)

Pyridine (10.60cm^3, 0.13mol) was added to a solution of **(22)** (10.00g, 62mmol) in diethyl ether (100cm^3). After cooling to below 0°C, thionyl chloride (9.75cm^3, 0.13mol) was added dropwise over 0.5h. The reaction mixture was allowed to warm to room temperature then stirred overnight before being filtered and washed with water. The organic layer was dried (sodium sulphate), filtered and evaporated *in vacuo* to give a brown oil which was adsorbed onto silica and column chromatographed using 40-60° petroleum ether-20% toluene/petroleum ether as eluant to give **(23)** as a yellow oil.

Yield=6.70g (54%)

NMR (^{1}H, $CDCl_3$, 270MHz): δ7.51-7.21 (5H, m); 6.58(1H, t, J=2.01, 1.83Hz); 4.30 (2H, dd, J=2.01Hz)

Microanalysis: Found; C, 61.8; H, 4.46; N, 0.10%. Calculated for $C_{10}H_8Cl_2$; C, 60.33; H, 4.05; N, 0%

4.6.2.3 Reaction of $PhCH(Cl)C{\equiv}CCH_2Cl$ (23) with $Ph_4P[MoCl(bipy)(CO)_3]$ (15) in $EtOH/H_2O$

A stirred suspension of $Ph_4P[MoCl(bipy)(CO)_3]$ (2.13g, 3.00mmol) in 30:1 (v:v) ethanol/water (31cm^3) was cooled to -78°C (acetone/dry-ice bath) and $PhCH(Cl)C{\equiv}CCH_2Cl$ (0.75g, 3.77mmol) was added dropwise. The mixture was slowly allowed to reach room temperature over 3h before being refrigerated and the resultant light-brown solid (**24**) filtered off and washed with ethanol followed by 40-60° petroleum ether.

Yield=1.03g

Infra-red: ν(C≡O) 2000, 1950, 1925cm^{-1}

NMR (^{1}H, DMSO-d^6, 270MHz): δ9.00-6.97 (~72H, m); 5.66 (1H, d, J=1.8Hz); 5.47 (1H, d, J=1.8Hz); 5.34 (1.7H, d, J=1.8Hz); 5.11 (1.7H, s); 4.39 (1H, t, J=1.8Hz); 4.29 (1.7H, d, J=2.0Hz); 1.06 (3H, t, J=7.0Hz)

Microanalysis: Found; C, 46.8; H, 3.05; N, 5.00%

4.6.2.4 Reaction of complex (24) with pyridine

The tricarbonyl solid (**24**) (75mg) was stirred with pyridine (0.20cm^3, 2.48mmol) in THF (5cm^3) for 18.5h. Following refrigeration and filtration, a red dicarbonyl containing solid (**25**) was obtained.

Yield=33mg

Infra-red: ν(C≡O) 1970, 1900cm^{-1}

NMR (^{1}H, DMSO-d^6, 270MHz): δ9.71-6.86 (~53H, m); 3.55 (1H, d, J=1.5Hz); 2.66 (1H, d, J=1.5Hz); 1.75 (0.3H, m); 1.06 (0.3H, t, J~6.7Hz)

Microanalysis: Found; C, 45.3; H, 3.14; N, 6.11%

4.6.3 Attempts to prepare unsubstituted η^3-butadienyl complexes

Attempts to prepare [MoCl(L$_2$)(CO)$_2$(η^3-CH$_2$CHCHCH$_2$Cl)] (L$_2$=bipy, (NCMe)$_2$)

4.6.3.1 Reaction of Ph$_4$P[MoCl(bipy)(CO)$_3$] with *cis*-1,4-dichloro-2-butene

A stirred suspension of Ph$_4$P[MoCl(bipy)(CO)$_3$] (1.00g, 1.41mmol) in methanol (20cm^3) was cooled to -9°C and *cis*-1,4-dichloro-2-butene (0.30cm^3, 2.85mmol) was added. The mixture was allowed to warm to room temperature over 1.5h, then stirred for a further 3.5h before being refrigerated overnight. The solid residue so produced was filtered, and washed with methanol, then 40-60° petroleum ether to give a dark brown solid (**26**) which was contaminated with [Mo(bipy)(CO)$_4$].

Yield=0.12g

Infra-red: ν(C≡O) 2040, 2000, 1980, 1920, 1875, 1815 cm^{-1}

(underlined values correspond to the carbonyl bands of [Mo(bipy)$(CO)_4$])

NMR (^1H, DMSO-d^6, 270MHz): δ9.72-7.63 (108H, m); 7.55 (1H, m); 7.13 (1H, m); 6.85 (1H, m); 4.54 (1H, m); 3.23 (6H, s); 2.30 (1H, m)

Microanalysis: Found; C, 40.3; H, 2.59; N, 6.94%.

Calculated for $C_{16}H_{14}Cl_2MoN_2O_2$; C, 44.37; H, 3.26; N, 6.47%

Reaction of Ph_4P[MoCl(bipy)$(CO)_3$] with *trans*-1,4-dichloro-2-butene

The reaction was repeated as above using *trans*-1,4-dichloro-2-butene to give a dark brown solid (**27**), which was again contaminated with [Mo(bipy)$(CO)_4$].

Yield=0.37g

Infra-red: ν(C≡O)2040, 2000, 1980, 1935, 1925, 1875, 1820cm^{-1}

(underlined values correspond to the carbonyl bands of [Mo(bipy)$(CO)_4$])

NMR (^1H, DMSO-d^6, 270MHz): δ9.71-7.66 (71H, m); 7.13 (1H, m); 6.85 (1H, m); 6.01 (1H, m); 4.26 (2.7H, m); 3.98 (1H, d, J=2.02Hz); 1.24 (1H, m); 0.85 (1H, m)

Microanalysis: Found; C, 37.9; H, 2.50; N, 6.78%.

Calculated for $C_{16}H_{14}Cl_2MoN_2O_2$; C, 44.37; H, 3.26; N, 6.47%

4.6.3.2 Reaction of [Mo(bipy)$(CO)_4$] with *cis*-1,4-dichloro-2-butene

To a stirred solution of [Mo(bipy)$(CO)_4$] (0.75g, 2.06mmol) in THF ($30cm^3$) was added *cis*-1,4-dichloro-2-butene ($2.20cm^3$, 20.90mmol). The reaction mixture was heated under reflux for 2h, before being cooled, refrigerated overnight and filtered to give a dark brown solid (**28**).

Yield=0.47g

Infra-red: ν(C≡O) 2025, 1950cm^{-1}

NMR (^{1}H, DMSO-d^6, 270MHz): δ9.47-7.63 (~11H, m); 6.07 (1H, s);
4.27 (partially obscured by water peak); 3.60 (1H, s); 2.21 (1H, s); 1.76 (1H, s)

Microanalysis: Found; C, 39.0; H, 2.89; N, 7.05%.
Calculated for $C_{16}H_{14}Cl_2MoN_2O_2$; C, 44.37; H, 3.26; N, 6.47%

Reaction of [Mo(bipy)(CO)$_4$] with *trans*-1,4-dichloro-2-butene

The reaction was repeated as above using *trans*-1,4-dichloro-2-butene to give a dark brown solid (**29**).

Yield=0.67g

Infra-red: ν(C≡O) 2025, 1950cm^{-1}

NMR (^{1}H, DMSO-d^6, 270MHz): similar to complex (**28**)

Microanalysis: Found; C, 36.4; H, 2.59; N, 7.20%

4.6.3.3 Reaction between [Mo(CO)$_6$] and *cis*-1,4-dichloro-2-butene in acetonitrile

Molybdenum hexacarbonyl (2.64g, 10.00mmol) and *cis*-1,4-dichloro-2-butene (5.00cm^3, 47.50mmol) were heated under reflux in acetonitrile (30cm^3) for 7.5h then cooled and stirred at room temperature overnight. Refrigeration of the reaction mixture followed by filtration gave a yellow powder (**30**) which was washed with 40-60° petroleum ether and dried and was subsequently shown to be [$MoCl_4(NCMe)_2$].

Yield=2.14g

Infra-red: no carbonyl bands; ν(C≡N) 2300, 2260cm^{-1}

4.6.3.4 Reaction between [Mo(NCMe)$_3$(CO)$_3$] and *cis*-1,4-dichloro-2-butene

Molybdenum hexacarbonyl (2.63g, 9.96mmol) was heated under reflux in acetonitrile for 17h. The resulting solution of [Mo(NCMe)$_3$(CO)$_3$] was cooled to -13°C and *cis*-1,4-dichloro-2-butene (2.50cm^3, 23.76mmol) added. The mixture was stirred for 2.25h then cooled and filtered and the product washed with 40-60° petroleum ether leaving a yellow powder (**31**).

Yield=1.07g

Infra-red: ν(C≡N) 2300cm^{-1}; ν(C≡O) 2000, 1970, 1955cm^{-1}

NMR (^{1}H, CD_3OD, 270MHz): δ6.35 (2H, m); 5.17 (2H, d, J=15.7Hz); 5.10 (2H, d, J=8.8Hz); 2.01 (3.3H, s)

Microanalysis: Found; C, 29.0; H, 2.53; N, 4.31%. Calculated for $C_9H_9Cl_2MoNO_3$; C, 31.20; H, 2.62; N, 4.05%

Attempts to prepare [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=CH$_2$}]

4.6.3.5 Preparation of [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (32)

Molybdenum hexacarbonyl (2.64g, 10.00mmol), 2,2'-bipyridyl (1.56g, 10.00mmol) and cinnamoyl chloride (3.30g, 20.00mmol) were heated under reflux in THF (35cm^3) for 4h before being cooled and the product filtered off and washed with THF followed by 40-60° petroleum ether to leave an orange-brown solid (**32**).

Yield=4.29g (90%)

Infra-red: ν(C≡O) 1965, 1900cm^{-1}; ν(C=O) 1730cm^{-1}

Microanalysis: Found; C, 52.4; H, 3.12; N, 6.25%. Calculated for $C_{21}H_{15}ClMoN_2O_3$; C, 53.12; H, 3.18; N, 5.90%.

4.6.3.6 Reaction of [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O)}] (32) with Ph_3P^+-CH_2^-

The dimethylsulphinyl anion was generated by treating DMSO (20cm^3) with a 50% sodium hydride/mineral oil dispersion (0.48g, 10.00mmol) and heating for 0.75h at 75°C. The solution was then cooled and methyltriphenylphosphonium bromide (3.57g, 10.00mmol) dissolved in DMSO (30cm^3) added. The resulting dark red phosphorus ylid solution was stirred for a further 0.25h before [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O)=}] (2.42g, 5.1mmol) was added. The mixture was stirred overnight, but the only identifiable product recovered was [Mo(bipy)(CO)$_4$].

4.6.3.7 Attempted Perkin reaction on [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (32)

A mixture of [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (1.00g, 2.11mmol), lead (II) oxide (0.25g, 1.12mmol) and glacial acetic acid (0.26cm^3, 4.54mmol) was heated under reflux in acetic anhydride (20cm^3) for 1h, then stirred at room temperature for 60h before being poured into water (40cm^3). After filtration a grey-green solid (0.17g) was isolated but exhibited no carbonyl bands in its infra-red spectrum.

4.6.3.8 Reaction of complex (32) with the anion of trimethylphosphonoacetate

Trimethylphosphonoacetate (0.68cm^3, 4.20mmol) and a 60% sodium hydride/mineral oil dispersion (0.17g, 4.25mmol) were stirred in THF (50cm^3) for 0.75h. Complex (**32**) [MoCl(bipy)(CO)$_2${η^3-(Ph)CHCHC=O}] (1.00g, 2.11mmol) was then added and the reaction mixture stirred for a further 20h at room temperature. An infra-red

spectrum of the reaction mixture taken after this time showed only [Mo(bipy)$(CO)_4$] and unreacted (**32**) and the reaction was consequently abandoned.

4.7.1 Preparation of [$MoCl_2$(NCMe)$(CO)_2(\eta^4$-CH_2=CH-CH=CH_2)] (33)

A solution of [Mo$(NCMe)_3(CO)_3$] was prepared by refluxing [Mo$(CO)_6$] (2.64g, 10.00mmol) in acetonitrile ($35cm^3$) for 2.5h. The solution was cooled to 0°C and 3,4-dichloro-1-butene ($2.20cm^3$, 20.24mmol) was added. The reaction mixture was then allowed to warm to room temperature and, after stirring for 1h, a yellow solid was precipitated. After overnight refrigeration, the reaction mixture was filtered and the yellow solid thus obtained was washed with 10:1 (v:v) acetonitrile/diethyl ether ($50cm^3$) and dried under suction to give complex (**33**) which is believed to have the above structure.

Yield=0.80-1.51g (30-50%)

Infra-red: ν(C≡N) 2313, 2284cm^{-1} ; ν(C≡O) 2015, 2004, 1952, 1935cm^{-1}

Infra-red (MeCN solution): ν(C≡O) 2022, 1952cm^{-1}

Microanalysis: Found; C, 30.00; H, 2.78; N, 4.32% (average of 3).

Calculated for $C_8H_9Cl_2MoNO_2$; C, 30.22; H, 2.85; N, 4.40%

4.7.2 Reaction of complex (33) with triphenylphosphine

To a stirred solution of complex (**33**) (325mg, ~1mmol) in acetonitrile was added, dropwise, triphenylphosphine (275mg, 1.05mmol) dissolved in dichloromethane ($8cm^3$). An infra-red spectrum taken of the reaction solution after 0.2h showed the presence in solution of a dicarbonyl species possessing carbonyl bands at 1939 and 1829cm^{-1}. The reaction solvent was removed *in vacuo* to leave a dark orange solid. Attempts to recrystallise this solid from a variety of solvent systems including chloroform with

cyclohexane, xylene or diethyl ether and acetonitrile/cyclohexane were unsuccessful and the data below therefore refers to the crude material obtained.

Yield=85mg

Infra-red: ν(C≡O) 2033(weak), 1921, 1817(both bands have shoulders)cm^{-1}

Microanalysis: Found; C, 59.40; H, 4.44; N, 1.20%. Calculated for $C_{24}H_{21}Cl_2MoO_2P$; C, 53.46; H, 3.93; N, 0%.

4.7.3 Reaction of complex (33) with methyldiphenylphosphine

To a stirred solution of complex **(33)** (332mg, ~1mmol) dissolved in acetonitrile (15ml) was added methyldiphenylphosphine (0.23cm^3, 1.1mmol). An infra-red spectrum of the reaction solution was taken after 0.2h and indicated the presence in solution of a dicarbonyl species with carbonyl bands centred at 1927 and 1825cm^{-1}. The volume of reaction solvent was reduced by about 2/3 and the reaction mixture refrigerated overnight. A precipitate appeared to have been formed but filtration yielded only an intractable dark-brown oil.

4.7.4 Reaction of complex (33) with dimethylphenylphosphine

The above procedure was repeated employing dimethylphenylphosphine. An infra-red spectrum taken of the reaction solution after 0.25h showed the presence in solution of a dicarbonyl species with carbonyl bands centred at 1935 and 1838cm^{-1}. Subsequent reduction of the reaction solvent volume following addition of the phosphine and overnight refrigeration led only to the recovery of an intractable dark-brown tar

4.7.5.1 Reaction of complex (33) with pyridine

To a stirred solution of complex (**33**) (328mg, ~1mmol), dissolved in acetonitrile ($15cm^3$) was added pyridine (few drops). A sandy-yellow solid precipitated from the reaction mixture after 0.2h and was filtered off, washed with diethyl ether ($30cm^3$) and dried to give (**34**).

Yield=235mg

Infra-red: $\nu(C\equiv O)$ 1919, $1817cm^{-1}$

Microanalysis: Found; C, 43.60; H, 3.75; N, 7.39%. Calculated for $C_{14}H_{16}Cl_2MoN_2O_2$; C, 40.54; H, 3.86; N, 6.75%

NMR (^1H, DMSO-d^6, 270MHz): δ8.75 (2H, br s); 8.17 (1H, m); 7.70 (2H, m); 6.35 (0.4H, m); 5.28 (0.5H, d); 5.15 (0.5H, d); 2.07 (~0.75H, s)

4.7.5.2 Reaction of complex (33) with 2-methoxypyridine

To a stirred solution of complex (**33**) (328mg, ~1mmol) in acetonitrile ($15cm^3$) was added 2-methoxypyridine (few drops). A yellow solid was precipitated from the reaction mixture after 0.5h and was filtered off, washed with diethyl ether ($30cm^3$) and dried. The solid proved to be non-carbonyl containing by infra-red and is believed to be $[Mo(NCMe)_3Cl_3]$ with other Mo containing impurities.

Yield=120mg

Infra-red: $\nu(C\equiv N)$ 2311, $2278cm^{-1}$

Microanalysis: Found; C, 19.80; H, 2.76; N, 11.30%. Calculated for $C_6H_9Cl_3MoN_3$; C, 22.14; H, 2.79; N, 12.91%

4.7.6 Reaction of complex (33) with 1,4-diphenyl-1,3-butadiene

A stirred mixture of complex (**33**) (335mg, ~1mmol) in acetonitrile (15ml) and 1,4-diphenyl-1,3-butadiene (230mg, 1.1mmol) dissolved in toluene (10ml) were heated under reflux for 0.6h, at which stage an infra-red spectrum taken showed carbonyl bands at 1919 and 1798cm^{-1}. The reaction mixture was cooled and the solvent reduced to about 1/3 the original volume. Overnight refrigeration followed by filtration yielded only a small amount of non-carbonyl containing solid and no further material could be obtained upon subsequent treatment of the reaction filtrate.

4.7.7 Reaction of complex (33) with diethylacetylenedicarboxylate

To a stirred solution of complex (**33**) (325mg, ~1mmol) in acetonitrile (15ml) was diethylacetylenedicarboxylate (190mg, 1.1mmol). Infra-red spectra were taken of the reaction mixture after 2, 3 and 4h stirring at room temperature. These showed two main carbonyl bands at 1987 and 1825cm^{-1} along with other weaker bands at 2023, 1948 and 1800cm^{-1}. After stirring for 4.5h, the reaction solvent was reduced to half-volume and the mixture refrigerated. Filtration yielded only a non-carbonyl containing solid and no other material could be isolated from the filtrate.

4.7.8 Reaction of complex (33) with diphenylacetylene

To a stirred solution of complex (**33**) (331mg, ~1mmol) in acetonitrile (15ml) was added dropwise diphenylacetylene (mg, mmol) dissolved in acetonitrile (5ml). The reaction turned a darker orange-brown over ~2h. An infra-red spectrum of the reaction mixture contained carbonyl bands centred at 2081, 2014 and 1950 cm^{-1}. The reaction solvent was removed *in vacuo* and the brown residue redissolved in dichloromethane.

Cyclohexane was then added and a small amount of solid isolated following refrigeration however this appeared to be a mixture of carbonyl species and further attempts at purification were unsuccessful.

Infra-red: ν(C≡N) 2363, 2311, 2278, 2253cm^{-1}; ν(C≡O) 2024, 1987, 1950, 1925, 1877, 1831cm^{-1}

4.7.9 Reaction of complex (33) with molecular bromine

To a stirred solution of complex (**33**) (1.00g, ~3mmol) in acetonirile (30cm^3) at -40°C (acetonitrile/solid CO_2 bath) was added dropwise molecular bromine (1.44g, 9mmol) in dichloromethane (10cm^3). The reaction solution was allowed to warm to room temperature over ~2h before being filtered through florisil. Column chromatography of the organic products on silica using 4:1 60-80° petroleum ether/ethyl acetate as eluant yielded a yellow oil (**35**) which was found to be a mixture of *cis* and *trans*-1,4-dibromo-2-butene.

Yield=0.30g(14%)

NMR (^{1}H, $CDCl_3$, 270MHz): δ5.88 (m, 2H); 5.80 (m, 4H); 3.94 (dd, J=1.8, 5.5Hz, 2H); 3.87 (dd, J=2.2, 4.4Hz, 1H)

NMR (^{13}C, $CDCl_3$, 68MHz): δ130.76, 129.79, 129.69, 129.63 (CH=CH); 37.80, 33.70, 30.85, 24.47 (CH_2Br) (assignments confirmed by a 135DEPT spectrum)

Microanalysis: Found; C, 18.7; H, 2.38%. Calculated for $C_4H_6Br_2$; C, 22.65; H, 2.85%

Mass spec.: M^+=213 (dibrominated)

4.7.10 Attempted preparation of $[MoCl_2(NCPr)(CO)_2(\eta^3\text{-}CH_2{=}CH\text{-}CH{=}CH_2)]$

The procedure for the preparation of complex (**33**) was followed, replacing MeCN with PrCN. No precipitate was forthcoming following the addition of 3,4-dichloro-1-butene and refrigeration of the reaction mixture led to the recovery of crystals of $[MoCl_3(NCPr)_3]$ (**36**) which were suitable for an X-ray diffraction study (see **Appendix 2**).

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APPENDIX 1

THE CRYSTAL STRUCTURE OF COMPLEX (9)

$Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$

Note on $Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$(9)

A crystal of approximate dimensions 0.15 x 0.15 x 0.35 mm was used for data collection. *Crystal data*: $C_{25}H_{47}O_9NMo_2$, M=697.5 monoclinic, a=12.768(3), b=15.898(4), c=15.879(4)Å, β=92.82(3), U=3219.4Å^3, space group $P2_1/c$, Z=4, D_c=1.44gcm^{-3}, μ(Mo-K_α)=8.1cm^{-1}, F(000)=1440. Data were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2\leq\theta\leq24°$. 7945 reflections were collected of which 2955 were unique with $I\geq3\sigma(I)$. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by Patterson methods and refined using the SHELX[1,2] suite of programs. In the final least squares cycles all the atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions (with a common isotropic thermal parameter of 0.12Å^2) in all cases except for the allyl termini, where the relevant hydrogens were located in an advanced difference Fourier map and ultimately refined at a fixed distance of 1.08Å from the appropriate carbons and with a common refined thermal parameter of 0.06Å^2. In the latter stages of convergence the anion and cation moieties were treated as separate blocks. Final residuals after 16 cycles of least squares were R=R_w=0.0303 for unit weights which gave the best convergence. Max. final shift/esd was 0.240. (This value related to one of the allylic hydrogen positional parameters whereas for other atom types, shift/esd values typically averaged 0.025). the max. and min. residual densities were 0.24 and -0.32eÅ^{-3} respectively. Final fractional atomic coordinates and isotropic thermal parameters, bond distances and angles are given in Tables 1, 4 and 5 respectively. Anisotropic temperature factors are shown in Table 3. The assymetric unit is shown overleaf along with the labelling scheme used.

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Complex (9):- $Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$

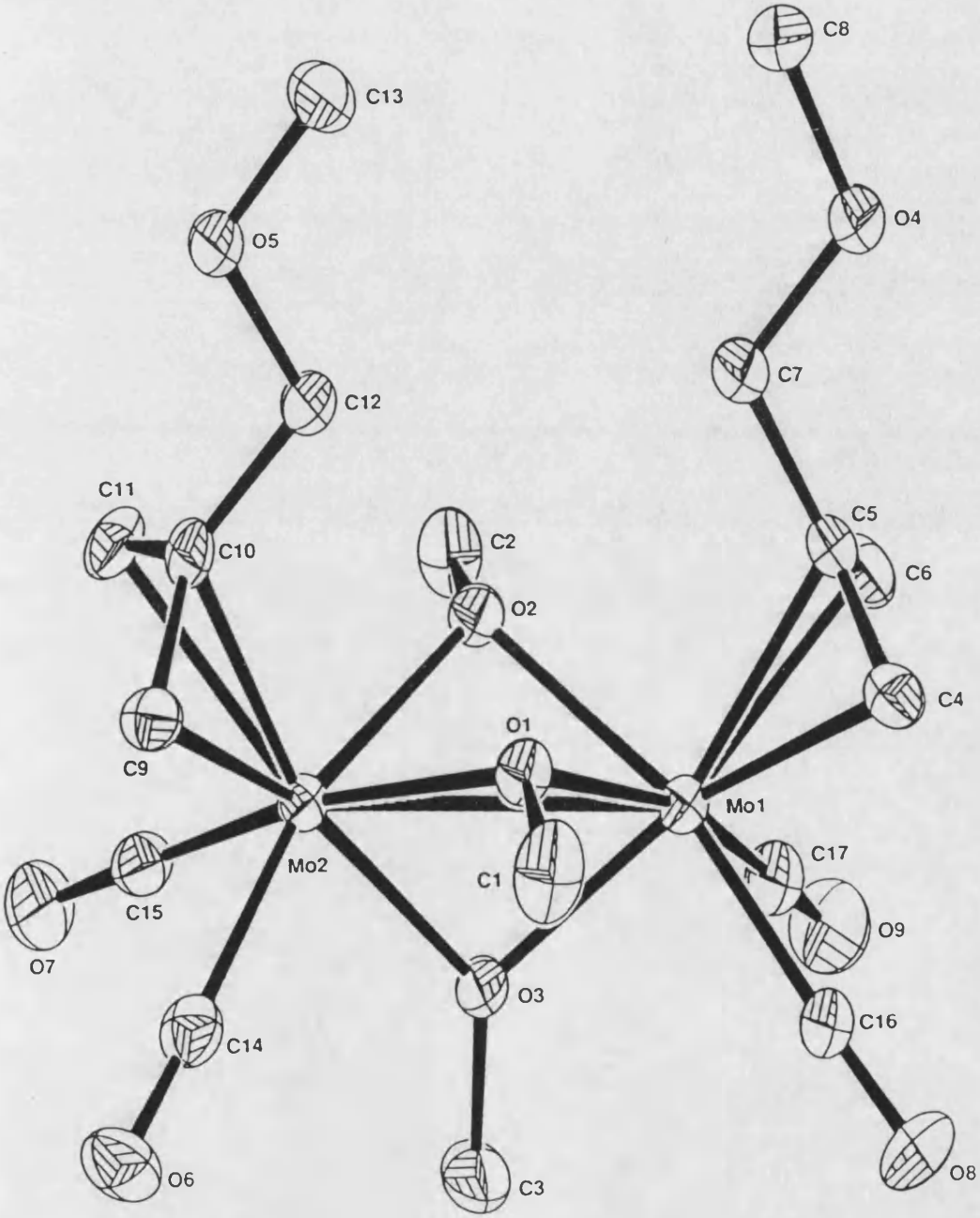

TABLE 1 Fractional atomic coordinates and thermal parameters (Å) for $Et_4N[Mo_2(CO)_4\{\eta^3\text{-}CH_2C(CH_2C(CH_2OMe)CH_2\}_2(\mu\text{-}OMe)_3]$(9)

Atom	x	y	z	Uiso or Ueq	(***)
Mo1	0.18346(4)	0.24075(3)	0.47820(3)	0.0355(3)	***
Mo2	-0.06139(4)	0.25303(3)	0.49445(3)	0.0335(3)	***
O1	0.0491(3)	0.2652(3)	0.3932(2)	0.038(2)	***
O2	0.0572(3)	0.1536(2)	0.5067(3)	0.037(2)	***
O3	0.0760(3)	0.3079(3)	0.5478(3)	0.045(3)	***
O4	0.2334(4)	0.0299(3)	0.3021(3)	0.065(3)	***
O5	-0.1864(3)	0.0721(3)	0.3033(3)	0.050(3)	***
O6	-0.1793(5)	0.4247(3)	0.5000(4)	0.079(4)	***
O7	-0.1751(4)	0.2508(4)	0.6636(3)	0.070(3)	***
O8	0.3275(5)	0.3959(3)	0.4537(4)	0.079(4)	***
O9	0.3347(4)	0.2299(4)	0.6373(3)	0.078(4)	***
C1	0.0452(6)	0.3312(5)	0.3335(5)	0.070(5)	***
C2	0.0645(6)	0.1000(5)	0.5785(5)	0.058(5)	***
C3	0.0922(6)	0.3731(5)	0.6070(6)	0.072(6)	***
C4	0.2773(6)	0.2246(5)	0.3579(5)	0.057(5)	***
C5	0.2504(5)	0.1462(4)	0.3936(4)	0.045(4)	***
C6	0.3004(6)	0.1278(4)	0.4733(5)	0.053(5)	***
C7	0.1745(5)	0.0868(4)	0.3502(5)	0.051(4)	***
C8	0.1710(6)	-0.0349(4)	0.2653(6)	0.064(5)	***
C9	-0.1969(5)	0.2598(4)	0.3917(4)	0.047(4)	***
C10	-0.1657(5)	0.1752(4)	0.4094(4)	0.039(4)	***
C11	-0.1860(6)	0.1456(4)	0.4908(5)	0.049(4)	***

TABLE 1 (cont.)

Atom	x	y	z	Uiso or Ueq	(***)
C12	-0.1097(5)	0.1238(4)	0.3471(4)	0.043(4)	***
C13	-0.1392(6)	0.0240(5)	0.2400(5)	0.059(5)	***
C14	-0.1344(6)	0.3619(5)	0.4956(5)	0.051(5)	***
C15	-0.1302(5)	0.2496(4)	0.6015(4)	0.046(4)	***
C16	0.2718(5)	0.3386(4)	0.4615(5)	0.051(4)	***
C17	0.2778(5)	0.2328(4)	0.5781(5)	0.053(4)	***
N1	0.5194(4)	0.0639(4)	0.2101(4)	0.056(4)	***
C18	0.4191(5)	0.0370(5)	0.1602(5)	0.058(5)	***
C19	0.4286(6)	-0.0409(5)	0.1063(6)	0.082(6)	***
C20	0.6031(5)	0.0923(5)	0.1498(5)	0.067(5)	***
C21	0.5733(7)	0.1651(6)	0.0931(6)	0.085(6)	***
C22	0.5663(6)	-0.0066(6)	0.2632(6)	0.080(6)	***
C23	0.4973(8)	-0.0438(7)	0.3285(7)	0.122(10)	***
C24	0.4857(6)	0.1371(5)	0.2646(5)	0.068(5)	***
C25	0.5746(7)	0.1782(7)	0.3171(7)	0.117(8)	***
H11	-0.0240(6)	0.3689(5)	0.3418(5)	0.111(8)	
H41	0.2333(45)	0.2410(43)	0.2997(25)	0.069(8)	
H42	0.3586(21)	0.2414(43)	0.3623(40)	0.069(8)	
H61	0.2701(60)	0.0898(38)	0.5223(35)	0.069(8)	
H62	0.2976(63)	0.0635(18)	0.4930(45)	0.069(8)	
H91	-0.1779(52)	0.2798(41)	0.3292(21)	0.069(8)	
H92	-0.2726(26)	0.2791(41)	0.4091(40)	0.069(8)	
H111	-0.1617(54)	0.0828(21)	0.5077(45)	0.069(8)	
H112	-0.2613(28)	0.1551(43)	0.5154(41)	0.069(8)	

TABLE 2 Fractional atomic coordinates for the hydrogen atoms

Atom	x	y	z
H12	0.0424	0.3053	0.2702
H13	0.1142	0.3701	0.3427
H21	-0.0130	0.0804	0.5945
H22	0.1016	0.1335	0.6315
H23	0.1108	0.0453	0.5644
H31	0.0178	0.3926	0.6300
H32	0.1290	0.4259	0.5772
H33	0.1423	0.3510	0.6594
H71	0.1199	0.1212	0.3089
H72	0.1320	0.0527	0.3966
H81	0.2195	-0.0761	0.2296
H82	0.1104	-0.0080	0.2236
H83	0.1354	-0.0704	0.3147
H121	-0.0510	0.0851	0.3796
H122	-0.0727	0.1645	0.3027
H131	-0.1980	-0.0148	0.2076
H132	-0.0790	-0.0156	0.2692
H133	-0.1048	0.0656	0.1950
H181	0.3975	0.0873	0.1168
H182	0.3578	0.0284	0.2042
H191	0.3547	-0.0543	0.0729
H192	0.4492	-0.0923	0.1487
H193	0.4888	-0.0334	0.0613
H201	0.6723	0.1092	0.1882

TABLE 2 (cont.)

Atom	x	y	z
H202	0.6207	0.0395	0.1099
H211	0.6377	0.1796	0.0538
H212	0.5564	0.2190	0.1317
H213	0.5049	0.1493	0.0534
H221	0.5859	-0.0571	0.2210
H222	0.6369	0.0168	0.2954
H241	0.5376	-0.0937	0.3632
H242	0.4265	-0.0683	0.2974
H243	0.4776	0.0056	0.3719
H241	0.4292	0.1136	0.3074
H242	0.4494	0.1846	0.2240
H251	0.5448	0.2289	0.3545
H252	0.6316	0.2027	0.2752
H253	0.6114	0.1317	0.3586

TABLE 3 Anisotropic thermal parameters (Å)

Atom	U11	U22	U33	U23	U13	U12
Mo1	0.0302(3)	0.0334(3)	0.0429(3)	-0.0037(3)	0.0013(2)	-0.0025(3)
Mo2	0.0311(3)	0.0311(3)	0.0383(3)	-0.0012(3)	0.0006(2)	0.0006(2)
O1	0.039(2)	0.037(2)	0.038(2)	0.009(2)	0.001(2)	0.000(2)
O2	0.037(2)	0.033(2)	0.040(3)	0.007(2)	0.000(2)	0.002(2)
O3	0.034(3)	0.046(3)	0.054(3)	-0.019(2)	0.000(2)	-0.005(2)
O4	0.042(3)	0.062(3)	0.090(4)	-0.036(3)	0.020(3)	-0.009(2)
O5	0.034(2)	0.050(3)	0.066(3)	-0.019(2)	-0.001(2)	-0.001(2)
O6	0.069(4)	0.048(3)	0.120(5)	-0.011(3)	-0.006(4)	0.023(3)
O7	0.073(3)	0.083(4)	0.055(3)	-0.008(3)	0.025(2)	-0.004(3)
O8	0.068(4)	0.054(3)	0.115(5)	-0.005(3)	0.021(3)	-0.027(3)
O9	0.063(3)	0.095(4)	0.076(4)	-0.014(3)	-0.029(3)	0.008(3)
C1	0.064(5)	0.076(5)	0.070(5)	0.038(4)	0.005(4)	0.004(4)
C2	0.055(5)	0.059(5)	0.059(5)	0.023(4)	0.005(4)	0.009(4)
C3	0.054(5)	0.078(6)	0.084(6)	-0.047(5)	-0.005(5)	0.001(4)
C4	0.050(4)	0.051(4)	0.068(5)	-0.011(4)	0.020(4)	-0.003(4)
C5	0.039(4)	0.041(4)	0.055(5)	-0.012(3)	0.012(3)	0.002(3)
C6	0.055(5)	0.048(4)	0.057(5)	-0.002(4)	0.006(4)	0.012(4)
C7	0.041(4)	0.051(4)	0.060(5)	-0.018(3)	0.008(3)	-0.001(3)
C8	0.057(5)	0.051(4)	0.083(6)	-0.023(4)	0.012(4)	-0.012(4)
C9	0.036(3)	0.048(4)	0.057(4)	-0.005(4)	-0.013(3)	0.007(3)
C10	0.027(3)	0.046(4)	0.042(4)	0.000(3)	-0.005(3)	0.000(3)
C11	0.037(4)	0.049(4)	0.063(5)	-0.004(3)	-0.001(4)	-0.014(3)
C12	0.033(4)	0.045(4)	0.052(4)	-0.011(3)	-0.002(3)	-0.003(3)
C13	0.049(5)	0.059(5)	0.069(6)	-0.020(4)	-0.004(4)	0.009(4)

TABLE 3 (cont.)

Atom	U11	U22	U33	U23	U13	U12
C14	0.044(4)	0.049(4)	0.060(5)	-0.002(3)	-0.007(4)	-0.001(4)
C15	0.044(4)	0.040(4)	0.054(4)	-0.004(4)	-0.004(3)	-0.002(3)
C16	0.037(4)	0.049(4)	0.066(5)	-0.008(4)	0.002(4)	-0.002(3)
C17	0.043(4)	0.053(4)	0.063(5)	-0.008(4)	-0.001(3)	-0.001(4)
N1	0.037(3)	0.068(4)	0.062(4)	-0.016(3)	-0.006(3)	0.015(3)
C18	0.031(4)	0.074(5)	0.069(5)	-0.011(4)	-0.008(3)	0.002(3)
C19	0.058(5)	0.090(6)	0.100(7)	-0.035(5)	-0.001(5)	-0.006(5)
C20	0.033(4)	0.080(5)	0.089(6)	-0.022(5)	0.013(4)	0.001(4)
C21	0.065(6)	0.092(6)	0.097(7)	0.000(5)	0.012(5)	-0.001(5)
C22	0.051(5)	0.096(6)	0.094(7)	0.011(5)	-0.003(5)	0.026(5)
C23	0.096(9)	0.145(10)	0.125(10)	0.058(8)	-0.009(7)	0.037(8)
C24	0.043(4)	0.080(5)	0.080(6)	-0.033(4)	0.004(4)	0.014(4)
C25	0.065(6)	0.151(10)	0.134(9)	-0.091(8)	-0.023(6)	0.023(6)

TABLE 4 Bond lengths (Å)

Mo1-Mo2	3.155(1)	Mo1-O1	2.160(4)
Mo1-O2	2.189(4)	Mo1-O3	2.092(4)
Mo1-C4	2.309(8)	Mo1-C5	2.210(7)
Mo1-C6	2.339(8)	Mo1-C16	1.946(7)
Mo1-C17	1.942(7)	Mo2-O1	2.192(4)
Mo2-O2	2.191(4)	Mo2-O3	2.099(4)
Mo2-C9	2.315(6)	Mo2-C10	2.220(6)
Mo2-C11	2.333(7)	Mo2-C14	1.966(7)
Mo2-C15	1.943(7)	O1-C1	1.411(9)
O2-C2	1.418(8)	O3-C3	1.404(9)
O4-C7	1.419(9)	O4-C8	1.410(9)
O5-C12	1.431(8)	O5-C13	1.416(9)
O6-C14	1.155(9)	O7-C15	1.161(8)
O8-C16	1.166(9)	O9-C17	1.156(9)
C1-H11	1.080(12)	C4-C5	1.417(10)
C4-H41	1.09(5)	C4-H42	1.07(3)
C5-C6	1.414(10)	C5-C7	1.495(9)
C6-H61	1.07(6)	C6-H62	1.07(4)
C9-C10	1.426(9)	C9-H91	1.07(4)
C9-H92	1.06(4)	C10-C11	1.404(10)
C10-C12	1.488(9)	C11-H111	1.07(4)
C11-H112	1.07(4)	H61-H62	0.73(9)
N1-C18	1.531(9)	N1-C20	1.533(10)
N1-C22	1.507(11)	N1-C24	1.523(10)
C18-C19	1.511(12)	C20-C21	1.500(12)
C22-C23	1.509(15)	C24-C25	1.520(12)

TABLE 5 Bond angles (°)

O1-Mo1-Mo2	43.9(1)	O2-Mo1-Mo2	43.9(1)
O2-Mo1-O1	70.8(1)	O3-Mo1-Mo2	41.2(1)
O3-Mo1-O1	73.3(2)	O3-Mo1-O2	72.9(2)
C4-Mo1-Mo2	129.1(2)	C4-Mo1-O1	86.4(2)
C4-Mo1-O2	121.1(2)	C4-Mo1-O3	150.3(2)
C5-Mo1-Mo2	120.3(2)	C5-Mo1-O1	93.8(2)
C5-Mo1-O2	90.3(2)	C5-Mo1-O3	161.3(2)
C5-Mo1-C4	36.5(3)	C6-Mo1-Mo2	133.4(2)
C6-Mo1-O1	127.3(2)	C6-Mo1-O2	89.9(2)
C6-Mo1-O3	147.7(2)	C6-Mo1-C4	61.9(3)
C6-Mo1-C5	36.1(3)	C16-Mo1-Mo2	123.0(2)
C16-Mo1-O1	102.7(2)	C16-Mo1-O2	166.1(2)
C16-Mo1-O3	93.6(2)	C16-Mo1-C4	69.5(3)
C16-Mo1-C5	102.6(3)	C16-Mo1-C6	103.5(3)
C17-Mo1-Mo2	121.0(2)	C17-Mo1-O1	163.4(2)
C17-Mo1-O2	103.0(2)	C17-Mo1-O3	90.2(2)
C17-Mo1-C4	109.6(3)	C17-Mo1-C5	101.8(3)
C17-Mo1-C6	66.7(3)	C17-Mo1-C16	79.7(3)
O1-Mo2-Mo1	43.1(1)	O2-Mo2-Mo1	43.9(1)
O2-Mo2-O1	70.2(2)	O3-Mo2-Mo1	41.1(1)
O3-Mo2-O1	72.6(2)	O3-Mo2-O2	72.8(2)
C9-Mo2-Mo1	130.9(2)	C9-Mo2-O1	88.3(2)
C9-Mo2-O2	125.8(2)	C9-Mo2-O3	147.5(2)
C10-Mo2-Mo1	118.9(2)	C10-Mo2-O1	89.8(2)
C10-Mo2-O2	92.4(2)	C10-Mo2-O3	159.9(2)

TABLE 5(cont.)

C10-Mo2-C9	36.6(2)	C11-Mo2-Mo1	129.0(2)
C11-Mo2-O1	120.6(2)	C11-Mo2-O2	86.6(2)
C11-Mo2-O3	150.5(2)	C11-Mo2-C9	62.1(3)
C11-Mo2-C10	35.8(3)	C14-Mo2-Mo1	121.8(2)
C14-Mo2-O1	104.6(2)	C14-Mo2-O2	163.7(2)
C14-Mo2-O3	91.0(2)	C14-Mo2-C9	68.2(3)
C14-Mo2-C10	103.1(3)	C14-Mo2-C11	108.8(3)
C15-Mo2-Mo1	124.1(2)	C15-Mo2-O1	166.2(2)
C15-Mo2-O2	104.1(2)	C15-Mo2-O3	93.9(2)
C15-Mo2-C9	104.9(2)	C15-Mo2-C10	103.1(3)
C15-Mo2-C11	70.4(3)	C15-Mo2-C14	77.4(3)
Mo2-O1-Mo1	92.9(1)	C1-O1-Mo1	123.4(4)
C1-O1-Mo2	123.4(4)	Mo2-O2-Mo1	92.2(1)
C2-O2-Mo1	121.6(4)	C2-O2-Mo2	121.5(4)
Mo2-O3-Mo1	97.7(2)	C3-O3-Mo1	130.3(4)
C3-O3-Mo2	131.8(4)	C8-O4-C7	112.5(5)
C13-O5-C12	110.4(5)	H11-C1-O1	109.5(8)
C5-C4-Mo1	68.0(4)	H41-C4-Mo1	114(3)
H41-C4-C5	115(3)	H42-C4-Mo1	117(3)
H42-C4-C5	117(4)	H42-C4-H41	117(5)
C4-C5-Mo1	75.6(4)	C6-C5-Mo	176.9(4)
C6-C5-C4	115.3(6)	C7-C5-Mo1	116.5(5)
C7-C5-C4	122.5(6)	C7-C5-C6	122.1(6)
C5-C6-Mo1	67.0(4)	H61-C6-Mo1	99(4)
H61-C6-C5	127(4)	H62-C6-Mo1	134(4)

TABLE 5 (cont.)

H62-C6-C5	116(4)	H62-C6-H61	40(5)
C5-C7-O4	107.4(5)	C10-C9-Mo2	68.1(3)
H91-C9-Mo2	117(3)	H91-C9-C10	113(3)
H92-C9-Mo2	119(3)	H92-C9-C10	118(3)
H92-C9-H91	114(5)	C9-C10-Mo2	75.3(4)
C11-C10-Mo2	76.5(4)	C11-C10-C9	115.7(6)
C12-C10-Mo2	114.4(4)	C12-C10-C9	121.7(6)
C12-C10-C11	122.4(6)	C10-C11-Mo2	67.7(4)
H111-C11-Mo2	119(3)	H111-C11-C10	118(4)
H112-C11-Mo2	121(4)	H112-C11-C10	120(3)
H112-C11-H111	107(5)	C10-C12-O5	107.3(5)
O6-C14-Mo2	176.6(7)	O7-C15-Mo2	176.3(6)
O8-C16-Mo1	177.4(6)	O9-C17-Mo1	178.5(6)
H62-H61-C6	70(6)	H61-H62-C6	70(5)
C20-N1-C18	110.8(5)	C22-N1-C18	112.2(6)
C22-N1-C20	107.1(5)	C24-N1-C18	104.6(5)
C24-N1-C20	110.5(6)	C24-N1-C22	111.7(6)
C19-C18-N1	115.4(6)	C21-C20-N1	115.7(6)
C23-C22-N1	116.3(7)	C25-C24-N1	114.4(6)

TABLE 6 Intermolecular distances (Å)

O5...H201	2.57	1	1.0	0.0	0.0
O5...H222	2.42	1	1.0	0.0	0.0
O5...H253	2.93	1	1.0	0.0	0.0
O5...H23	2.93	-1	0.0	0.0	1.0
O6...H32	2.76	-1	0.0	1.0	1.0
O6...H191	2.49	2	0.0	-1.0	0.0
O7...H83	2.93	-1	0.0	0.0	1.0
O7...H122	2.84	-2	0.0	1.0	0.0
O7...H91	2.66	-2	0.0	1.0	0.0
O7...H201	2.99	-2	1.0	1.0	0.0
O8...H193	2.62	2	1.0	-1.0	0.0
O8...H202	2.59	2	1.0	-1.0	0.0
O8...H181	2.70	-2	0.0	1.0	0.0
O8...H213	2.79	-2	0.0	1.0	0.0
O9...H241	2.71	-1	1.0	0.0	1.0
O9...H41	2.97	-2	0.0	1.0	0.0
O9...H212	2.95	-2	0.0	1.0	0.0
O9...H242	2.38	-2	0.0	1.0	0.0
C1...H132	2.97	2	0.0	-1.0	0.0
H11...C8	2.90	2	0.0	-1.0	0.0
H11...H82	2.45	2	0.0	-1.0	0.0
H13...C13	2.80	2	0.0	-1.0	0.0
C2...H132	2.75	-1	0.0	0.0	1.0
H23...H111	2.44	-1	0.0	0.0	1.0
C3...H82	2.83	-2	0.0	1.0	0.0

TABLE 6 (cont.)

H72...H111	2.65	-1	0.0	0.0	1.0
H81...H91	2.52	2	0.0	0.0	0.0
C9...H252	2.94	1	1.0	0.0	0.0
C10...H253	3.00	1	1.0	0.0	0.0
C13...H201	2.85	1	1.0	0.0	0.0
H92...C25	2.86	1	1.0	0.0	0.0
H92...H251	2.57	1	1.0	0.0	0.0

TABLE 7 Intramolecular distances (Å)

Mo1...H41	2.92	Mo1...H42	2.96
Mo1...H61	2.72	Mo2...H91	2.97
Mo2...H92	2.98	O1...O2	2.52
O1...O3	2.54	O1...H11	2.04
O1...H12	2.04	O1...H13	2.04
O1...H71	2.82	O1...H122	2.61
O1...H41	2.86	O2...O3	2.55
O2...H21	2.05	O2...H22	2.05
O2...H23	2.05	O2...H72	2.58
O2...H121	2.62	O2...H61	2.90
O3...H31	2.04	O3...H32	2.04
O3...H33	2.03	O3...C14	2.90
O3...C15	2.95	O3...C16	2.94
O3...C17	2.86	O4...C5	2.35
O4...H71	2.06	O4...H72	2.06
O4...H81	2.04	O4...H82	2.04
O4...H83	2.04	O4...H182	2.27
O4...H242	2.92	O4...H241	2.83
O5...C10	2.35	O5...H121	2.07
O5...H122	2.07	O5...H131	2.05
O5...H132	2.05	O5...H133	2.05
O6...H92	2.94	O7...H112	2.96
O8...H42	2.89	O9...H61	2.97
C1...H41	2.87	C1...H91	2.96
H11...H12	1.76	H11...H13	1.76

TABLE 7 (cont.)

H11...C9	2.94	H11...C14	2.87
H11...H91	2.42	H13...C16	2.73
C2...H61	2.82	H21...C11	2.88
H21...H111	2.29	H22...C17	2.91
H23...H61	2.28	H31...C14	2.85
H31...C15	2.98	H32...C16	2.99
H33...C17	2.90	C4...C6	2.39
C4...C7	2.55	C4...H71	2.68
C4...C16	2.44	C4...H241	2.77
C5...H71	2.12	C5...H72	2.12
C5...H41	2.12	C5...H42	2.12
C5...H61	2.23	C5...H62	2.11
C5...H241	2.76	C6...C7	2.55
C6...H72	2.69	C6...C17	2.38
C6...H42	2.65	C7...C8	2.35
C7...H82	2.60	C7...H83	2.60
C7...H121	2.94	C7...H41	2.70
C7...H61	2.93	C7...H62	2.71
H71...C8	2.66	H71...H41	2.40
H72...C8	2.57	H72...H61	2.65
H72...H62	2.55	C8...H182	2.80
C9...C11	2.40	C9...C12	2.55
C9...H122	2.65	C9...C14	2.42
C9...H112	2.73	C10...H121	2.12

TABLE 7 (cont.)

C10...H122	2.12	C10...H91	2.09
C10...H92	2.14	C10...H111	2.14
C10...H112	2.14	C11...C12	2.53
C11...H121	2.70	C11...C15	2.49
C11...H92	2.69	C12...C13	2.34
C12...H132	2.57	C12...H133	2.58
C12...H91	2.64	C12...H111	2.73
H121...C13	2.61	H121...H111	2.52
H122...C13	2.57	H122...H91	2.32
C14...C15	2.44	C14...H91	2.96
C14...H92	2.55	C15...H112	2.59
C16...C17	2.49	C16...H42	2.50
C17...H61	2.44	H41...H42	1.84
H42...C24	2.83	H42...H241	2.40
H42...H251	2.40	H91...H92	1.79
H92...H112	2.59	H111...H112	1.72
N1...H181	2.12	N1...H182	2.14
N1...C19	2.57	N1...H192	2.80
N1...H193	2.82	N1...H201	2.12
N1...H202	2.13	N1...C21	2.57
N1...H212	2.81	N1...H213	2.82
N1...H221	2.11	N1...H222	2.10
N1...C23	2.56	N1...H242	2.81
N1...H243	2.79	N1...H241	2.12

TABLE 7 (cont.)

N1...H242	2.13	N1...C25	2.56
N1...H252	2.80	N1...H253	2.79
C18...H191	2.14	C18...H192	2.10
C18...H193	2.15	C18...C20	2.52
C18...H202	2.73	C18...H213	2.72
C18...C22	2.52	C18...H221	2.74
C18...H242	2.74	C18...C24	2.42
C18...H241	2.62	C18...H242	2.57
H181...C19	2.09	H181...C20	2.65
H181...C21	2.60	H181...C24	2.66
H182...C19	2.14	H182...C22	2.83
H182...C23	2.83	H182...C24	2.53
C19...H202	2.76	C19...H221	2.65
H192...C22	2.66	H192...C23	2.98
H193...C20	2.81	C20...H211	2.12
C20...H212	2.12	C20...H213	2.13
C20...C22	2.45	C20...H221	2.64
C20...H222	2.61	C20...C24	2.51
C20...H242	2.76	C20...H252	2.66
H201...C21	2.11	H201...C22	2.60
H201...C24	2.76	H201...C25	2.67
H202...C21	2.10	H202...C22	2.65
C21...H242	2.68	C21...H252	2.99
H212...C24	2.66	H212...C25	3.00

TABLE 7 (cont.)

C22...H241	2.15	C22...H242	2.13
C22...H243	2.11	C22...C24	2.51
C22...H241	2.71	C22...H253	2.71
H221...C23	2.10	H222...C23	2.11
H222...C24	2.74	H222...C25	2.71
C23...H241	2.67	H243...C24	2.70
C24...H251	2.15	C24...H252	2.13
C24...H253	2.13	H241...C25	2.12
H242...C25	2.12		

APPENDIX 2

THE CRYSTAL STRUCTURE OF COMPLEX (36)

$[MoCl_3(NCPr)_3]$

Note on $[MoCl_3(NCPr)_3]$ (36)

A crystal of approximate dimensions 0.4 x 0.3 x 0.3mm was used for data collection.

Crystal data: $C_{12}H_{21}N_3Cl_3Mo$, M=409.6 monoclinic, a=19.939(5), b=11.885(3), c=16.296(3)Å, β=94.93(2)°, U=3847.5Å^3, space group $C2/c$, Z=8, D_c=1.41gcm^{-3}, μ(Mo-K_α)=10.8cm^{-1}, F(000)=1656. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2\leq\theta\leq24°$. 2581 reflections were collected of which 1771 were unique with $I\geq2\sigma(I)$. Data were corrected for Lorentz and polarization but not for absorption. The structure was solved by Patterson methods and refined using the SHELX[1,2] suite of programs. In the final least squares cycles all atoms were allowed to vibrate anisotropically. C12 was seen to exhibit 58% disorder with it's primed analogue. Hydrogen atoms were included at calculated positions except in the case of C11 and C12 due to the aforementioned disorder. Final residuals after 10 cycles of least squares were R=0.0420, R_w=0.0466, for a weighting scheme of w=1.7487/[σ^2(F) + 0.002293(F)^2]. Max. final shift/esd was 0.001. The max. and min. residual densities were 0.20 and -0.14eÅ^{-3} respectively. Final fractional atomic coordinates and isotropic thermal parameters, bond distances and angles are given in Tables 1, 5 and 6 respectively. Anisotropic temperature factors are shown in Table 3. The assymetric unit is shown overleaf, along with the labelling scheme used.

1. Sheldrick, G. M., SHELX86, a computer program for crystal structure determination, University of Göttingen, 1986

2 Sheldrick, G. M., SHELX76, a computer program for crystal structure determination, University of Cambridge, 1976

Complex (36):- $[MoCl_3(NCPr)_3]$

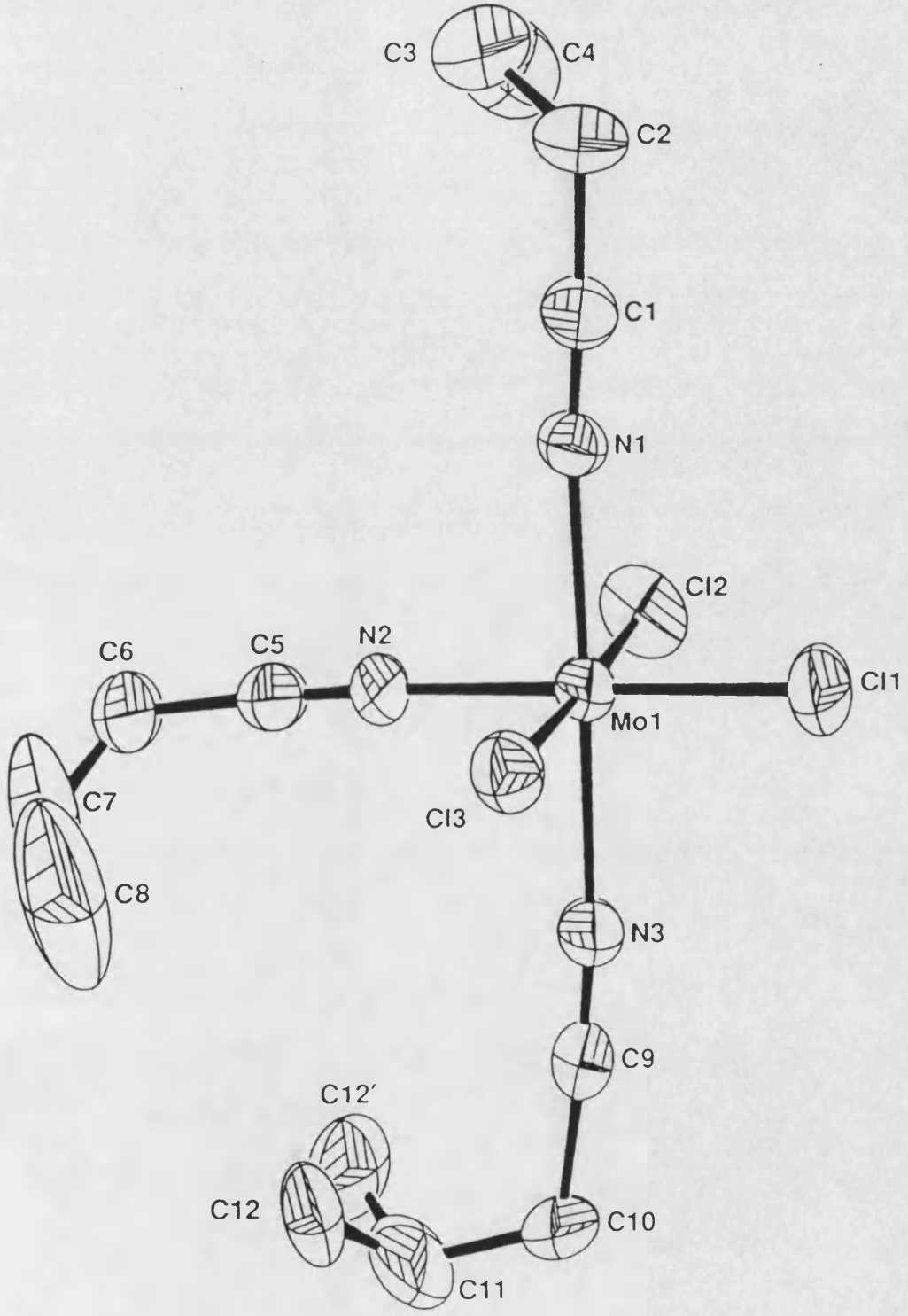

TABLE 1 Fractional atomic co-ordinates ($x10^4$) and equivalent isotropic temperature factors ($Å^2$ $x10^3$) for complex (36) $[MoCl_3(NCPr)_3]$

	x	y	z	U
Mo(1)	6797	4890	3667	71
Cl(1)	5971(1)	3469(2)	3734(1)	111(1)
Cl(2)	6118(1)	6234(2)	4307(1)	118(1)
Cl(3)	7562(1)	3655(2)	3051(1)	101(1)
N(1)	6352(3)	5367(4)	2484(3)	83(2)
N(2)	7549(3)	6169(5)	3611(3)	84(2)
N(3)	7263(3)	4467(5)	4844(4)	90(2)
C(1)	6053(4)	5591(5)	1891(4)	86(3)
C(2)	5690(4)	5924(7)	1098(4)	110(3)
C(3)	5776(6)	7180(9)	943(6)	148(5)
C(4)	5543(6)	7871(8)	1588(8)	181(6)
C(5)	7953(4)	6817(6)	3618(4)	86(3)
C(6)	8502(4)	7674(6)	3651(5)	115(3)
C(7)	9156(7)	7220(13)	3660(13)	240(11)
C(8)	9382(7)	6309(17)	3598(16)	329(17)
C(9)	7548(3)	4317(6)	5456(5)	91(3)
C(10)	7957(4)	4216(7)	6266(4)	113(3)
C(11)	8615(7)	4898(16)	6264(8)	175(8)
C(12)	9001(13)	4958(37)	5616(24)	194(21)
C(12')	8560(14)	5909(20)	6095(14)	154(11)

TABLE 2 Fractional atomic co-ordinates ($x10^4$)

	x	y	z
Mo(1)	6797	4890	3667
Cl(1)	5971(1)	3469(2)	3734(1)
Cl(2)	6118(1)	6234(2)	4307(1)
Cl(3)	7562(1)	3655(2)	3051(1)
N(1)	6352(3)	5367(4)	2484(3)
N(2)	7549(3)	6169(5)	3611(3)
N(3)	7263(3)	4467(5)	4844(4)
C(1)	6053(4)	5591(5)	1891(4)
C(2)	5690(4)	5924(7)	1098(4)
C(3)	5776(6)	7180(9)	943(6)
C(4)	5543(6)	7871(8)	1588(8)
C(5)	7953(4)	6817(6)	3618(4)
C(6)	8502(4)	7674(6)	3651(5)
C(7)	9156(7)	7220(13)	3660(13)
C(8)	9382(7)	6309(17)	3598(16)
C(9)	7548(3)	4317(6)	5456(5)
C(10)	7957(4)	4216(7)	6266(4)
C(11)	8615(7)	4898(16)	6264(8)
C(12)	9001(13)	4958(37)	5616(24)
C(12')	8560(14)	5909(20)	6095(14)

TABLE 3 Anisotropic temperature factors (Å x10^3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	66	84	62	5	-4	-4
Cl(1)	95(1)	124(1)	113(1)	7(1)	2(1)	-36(1)
Cl(2)	105(1)	140(2)	107(1)	-33(1)	4(1)	21(1)
Cl(3)	92(1)	106(1)	105(1)	0(1)	11(1)	16(1)
N(1)	78(3)	97(4)	70(3)	6(3)	-13(3)	6(3)
N(2)	78(3)	92(4)	80(4)	12(3)	-9(3)	-20(3)
N(3)	82(4)	121(4)	63(3)	15(3)	-11(3)	-12(3)
C(1)	97(5)	88(4)	72(4)	-10(3)	-5(4)	16(4)
C(2)	132(6)	121(6)	72(4)	-8(4)	-22(4)	41(5)
C(3)	180(9)	154(9)	105(7)	22(6)	-6(6)	24(7)
C(4)	171(9)	120(7)	243(14)	-21(8)	-36(9)	40(7)
C(5)	91(5)	85(4)	78(4)	12(3)	-10(3)	0(4)
C(6)	119(6)	99(5)	121(6)	23(4)	-29(5)	-40(5)
C(7)	112(10)	194(15)	426(27)	-67(17)	82(14)	-60(10)
C(8)	112(9)	217(18)	667(46)	-51(24)	88(17)	-3(11)
C(9)	85(4)	96(5)	92(5)	15(4)	3(4)	-14(3)
C(10)	123(6)	132(6)	80(5)	43(4)	-22(4)	-7(5)
C(11)	122(9)	271(18)	124(9)	23(9)	-47(8)	-46(10)
C(12)	81(15)	312(54)	185(34)	81(30)	-3(17)	-65(21)
C(12')	188(23)	120(15)	148(17)	6(12)	-14(15)	-53(14)

The temperature factor exponent takes the form:

$-2\ (U\ .h\ .a^* + \ \ldots\ \ +2U\ .h.k.a^*.b^*)$

TABLE 4 Hydrogen fractional atomic co-ordinates ($x10^4$) and isotropic temperature factors ($Å^2$ $x10^3$)

	x	y	z	U
H(21)	5865(4)	5506(7)	660(4)	298(21)
H(22)	5219(4)	5759(7)	1114(4)	298(21)
H(31)	5526(6)	7372(9)	433(6)	298(21)
H(32)	6245(6)	7331(9)	902(6)	298(21)
H(41)	5609(6)	8650(8)	1460(8)	298(21)
H(42)	5793(6)	7692(8)	2101(8)	298(21)
H(43)	5073(6)	7733(8)	1632(8)	298(21)
H(61)	8477(4)	8115(6)	4141(5)	298(21)
H(62)	8428(4)	8150(6)	3176(5)	298(21)
H(71)	9362(7)	7465(13)	4183(13)	298(21)
H(72)	9345(7)	7630(13)	3228(13)	298(21)
H(81)	9865(7)	6352(17)	3641(16)	298(21)
H(82)	9225(7)	6000(17)	3073(16)	298(21)
H(83)	9241(7)	5835(17)	4028(16)	298(21)
H(101)	7699(4)	4496(7)	6694(4)	298(21)
H(102)	8065(4)	3439(7)	6369(4)	298(21)

TABLE 5 Bond lengths (Å)

Cl(1)-Mo(1)	2.368(4)	Cl(2)-Mo(1)	2.391(4)
Cl(3)-Mo(1)	2.399(4)	N(1)-Mo(1)	2.128(8)
N(2)-Mo(1)	2.144(7)	N(3)-Mo(1)	2.120(8)
C(1)-N(1)	1.123(8)	C(5)-N(2)	1.113(8)
C(9)-N(3)	1.118(9)	C(2)-C(1)	1.480(11)
C(3)-C(2)	1.526(13)	C(4)-C(3)	1.443(15)
C(6)-C(5)	1.492(11)	C(7)-C(6)	1.409(15)
C(8)-C(7)	1.182(17)	C(10)-C(9)	1.496(11)
C(11)-C(10)	1.542(16)	C(12)-C(11)	1.360(37)
C(12')-C(11)	1.236(20)	C(12')-C(12)	1.666(43)

TABLE 6 Bond angles (°)

Cl(2)-Mo(1)-Cl(1)	92.0(2)	Cl(3)-Mo(1)-Cl(1)	93.1(2)
Cl(3)-Mo(1)-Cl(2)	174.8(1)	N(1)-Mo(1)-Cl(1)	89.7(2)
N(1)-Mo(1)-Cl(2)	90.6(3)	N(1)-Mo(1)-Cl(3)	90.9(3)
N(2)-Mo(1)-Cl(1)	179.6(1)	N(2)-Mo(1)-Cl(2)	88.2(3)
N(2)-Mo(1)-Cl(3)	86.7(3)	N(2)-Mo(1)-N(1)	90.6(3)
N(3)-Mo(1)-Cl(1)	92.4(3)	N(3)-Mo(1)-Cl(2)	89.1(3)
N(3)-Mo(1)-Cl(3)	89.3(3)	N(3)-Mo(1)-N(1)	177.9(2)
N(3)-Mo(1)-N(2)	87.2(3)	C(1)-N(1)-Mo(1)	172.5(6)
C(5)-N(2)-Mo(1)	176.7(5)	C(9)-N(3)-Mo(1)	173.9(6)
C(2)-C(1)-N(1)	176.9(8)	C(3)-C(2)-C(1)	110.6(8)
C(4)-C(3)-C(2)	112.8(10)	C(6)-C(5)-N(2)	178.4(7)
C(7)-C(6)-C(5)	114.5(9)	C(8)-C(7)-C(6)	135.2(14)
C(10)-C(9)-N(3)	175.0(7)	C(11)-C(10)-C(9)	110.7(8)
C(12)-C(11)-C(10)	124.6(19)	C(12')-C(11)-C(10)	116.9(18)
C(12')-C(11)-C(12)	79.7(20)	C(12')-C(12)-C(11)	46.9(15)
C(12)-C(12')-C(11)	53.4(16)		

TABLE 7 Selected intramolecular non-bonded distances (Å)

C(1)-Mo(1)	3.245	C(5)-Mo(1)	3.256
C(9)-Mo(1)	3.234	Cl(2)-Cl(1)	3.422
Cl(3)-Cl(1)	3.459	N(1)-Cl(1)	3.176
N(3)-Cl(1)	3.244	N(1)-Cl(2)	3.216
N(2)-Cl(2)	3.161	N(3)-Cl(2)	3.170
N(1)-Cl(3)	3.231	N(2)-Cl(3)	3.125
N(3)-Cl(3)	3.181	N(2)-N(1)	3.038
C(2)-N(1)	2.602	C(3)-N(1)	3.431